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CO-OPERATIVE MASS SPECTROMETRIC ANALYSIS OF C_1–C_4 HYDROCARBON MIXTURES

By J. BLEARS * and J. D. WALDRON *

SUMMARY

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One or more samples of each of the four mixtures listed in Table I were run on each instrument within a period of one or two days. The peak heights at selected mass numbers in the mixture spectrum of each sample were measured, and a set of simultaneous equations of the following form was set up and solved :

$$\Sigma c_{ij} s_j p_j = M_i$$

where c_{ij} is the cracking pattern of component j at peak i; s_j is the sensitivity coefficient of component j; p_j is the partial pressure of component j in the reservoir; M_i is the mixture peak height at mass i.

TABLE I

Special Method of Computation

Mixture	Components	Composition, mole %	Peak used for solution
1	*n*-Butane	50·0	Monoisotopic 43
	trans-2-Butene	50·0	56
2	Propane	10·0	Monoisotopic 44
	*iso*Butane	29·9	Monoisotopic 43
	*iso*Butene	60·1	56
3	Propane	20·0	Monoisotopic 44
	*iso*Butane	29·9	Monoisotopic 43
	1-Butene	30·1	56
	Propene	20·0	42
4	Propane	15·2	Monoisotopic 44
	n-Butane	9·9	Split on monoisotopic
	*iso*Butane	9·9	43 and 58
	1-Butene	15·1	56
	Propene	15·1	42
	Ethane	20·0	30
	Methane	14·8	16

* Research Department, Metropolitan Vickers Electrical Co. Ltd. MS received 26 May 1953.

† The Physical Chemistry Laboratory, The University, Oxford.
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SUMMARY

In order to establish figures for the accuracy of sector type mass spectrometers of British manufacture on hydrocarbon analysis, four synthetic C_1–C_4 paraffin–olefin mixtures were analysed several times on each of eight instruments. When the results were computed on the assumption that only the blended components were present in the mixtures, the average difference per component between the calculated and blended composition on the average instrument was 0·40 mole per cent. A general method of computation introduced slightly larger differences and, in addition, indicated the presence of small amounts of gases that were known to be absent from the blends. The results are presented in tabular form, and are compared with the results of a similar co-operative analysis programme reported by Starr and Lane.

INTRODUCTION

A CONSIDERABLE amount of information on the accuracy of the mass spectrometer in the analysis of hydrocarbon mixtures has been published.[1-3] Since most of this data relates to work carried out in the U.S.A. on 180° instruments, whereas in Europe most instruments are of the sector type, a co-operative analysis programme was organized by the Institute of Petroleum (Hydrocarbon Research Group—Mass Spectrometry Panel) with the object of establishing figures for the accuracy of analysis on sector type mass spectrometers, employing the conventional Nier type ion source. This paper presents the results of this programme in which, in all, 140 samples of four synthetic C_1–C_4 hydrocarbon mixtures were analysed by the eight participating laboratories.†

The Metropolitan-Vickers type M.S.2 mass spectrometer was used exclusively. The instruments were not specially prepared for the analyses, some had newly-cleaned ion sources, others had sources which had been operating for several months. The synthetic blends were prepared in Amsterdam by the Royal Dutch–Shell Group and their composition was known to the nearest 0·1 mole per cent.

METHOD OF ANALYSIS

Each mass spectrometer was calibrated with pure samples of all the C_1–C_4 paraffins and olefins, hydrogen, oxygen, nitrogen, and carbon dioxide, and for each component a cracking pattern and a sensitivity coefficient were determined. The cracking pattern of a compound lists the ratios of the intensities of the ion currents at the various mass numbers to the intensity of some reference peak, usually the largest peak in the spectrum. The sensitivity coefficient relates the intensity of the ion current at the reference peak to the pressure of sample in the sample reservoir.

One or more samples of each of the four mixtures listed in Table I were run on each instrument within a period of one or two days. The peak heights at selected mass numbers in the mixture spectrum of each sample were measured, and a set of simultaneous equations of the following form was set up and solved :

$$\Sigma c_{ij} s_j p_j = M_i$$

where c_{ij} is the cracking pattern of component j at peak i; s_j is the sensitivity coefficient of component j; p_j is the partial pressure of component j in the reservoir; M_i is the mixture peak height at mass i.

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The resulting partial pressures, p_j, were normalized, that is, each p_j value was divided by their sum in order to obtain the mole per cent composition of the various components in the mixture.

In some laboratories this programme was repeated after an interval of several weeks.

METHOD OF COMPUTATION

Since the analysis of a hydrocarbon mixture with the mass spectrometer involves the solution of a number of linear simultaneous equations, the values obtained for the concentrations of individual components are not completely independent, and errors in the determination of one component or in its cracking pattern are reflected in the values obtained for other components. When the composition is known approximately these effects can be reduced to a minimum by a careful selection of the peaks used in the calculation. When the mixture composition is unknown it is necessary to include equations for every possible component, and the overall accuracy is usually decreased, particularly if some of the additional equations are "ill conditioned."

It is clear that in this work, which is concerned with establishing the accuracy of the instrument, such errors should be avoided, and the computational method used should be that which gives the most accurate analysis. Accordingly, all the samples were calculated by the special methods given in Table I, which were based on the known composition of each synthetic blend. The peaks were chosen to give the best conditioned set of equations, bearing in mind the stability of the cracking pattern at the various mass numbers.

It is also important to know what accuracy can be obtained in the more practical case where the composition of the sample is unknown, and a number of the samples were recalculated as though they were unknown C_1–C_4 paraffin–olefin mixtures which might also contain the simpler inorganic gases, hydrogen, oxygen, nitrogen, and carbon dioxide, using the general method summarized in Table II. Some of the samples were not computed by this method because of the lack of complete calibration data on some instruments.

TABLE II

The General Method of Computation

The computation was carried out in the following order:

Component	Peak used for solution
Carbon dioxide	22
Propane	Monoisotopic 44
n-Butane	Split on monoisotopic 43 and 58
*iso*Butane	
Propene	Solve 4 equations on 41–42–55–56
1-Butene	
2-Butenes	
*iso*Butene	
Oxygen	32
Ethane	30
Ethylene	Best fit on 26 and 27
Nitrogen	28
Methane	16
Hydrogen	2

Using the general method of computation, small positive and negative values were obtained for the concentration of gases known to be absent from the blends. Though in normal practice the negative values are usually rejected, on the grounds that there cannot be a negative concentration, all such values were included in this work in order to obtain complete data on the distribution of the errors.

METHOD OF TREATING THE RESULTS

In order to assess the precision and accuracy of the mass spectrometric method as a whole, the analyses on each mixture were averaged over all instruments, and two parameters, d and σ, were calculated for each component in the mixture. For a particular component, d is the difference between the average analysis a, taken over all instruments, and the synthetic composition a_s, and is taken as a measure of the accuracy of the mass spectrometric method in the determination of that component. The standard deviation, σ, which was calculated from the expression

$$\sigma^2 = \Sigma(x - a)^2/n - 1$$

where x is any individual value and n is the total number of observations, provides a measure of the consistency of the method and of the reliability of a as the true mean value. Thus, for any component, these two parameters taken together show whether there is any systematic error inherent in the mass spectrometric determination of that component. A pictorial representation of the various terms used is given in Fig 1. Though, in general, the analyses

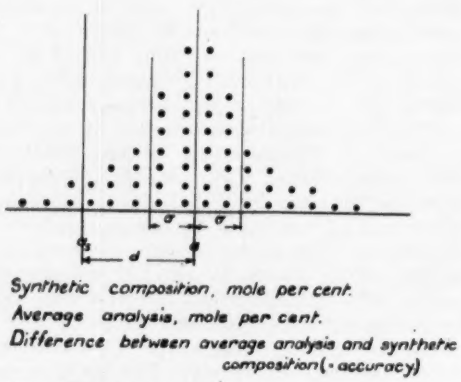
σ
σ
a_s
d
a_s = Synthetic composition, mole per cent.
a = Average analysis, mole per cent.
d = Difference between average analysis and synthetic composition (= accuracy)
σ = Standard deviation.

FIG 1

HYPOTHETICAL DISTRIBUTION CURVE ILLUSTRATING MEANING OF TERMS USED

were not distributed round the mean value in a Gaussian manner, the distributions were not so abnormal as to seriously affect the main conclusions. Typical distributions are shown in Fig 2.

The parameters d and σ are concerned only with the accuracy of the mass spectrometric method as a whole, and do not give a direct measure of the accuracy that is likely to be obtained in the more practical case where the sample is analysed on a single instrument. To estimate the latter accuracy, a further quantity d_i

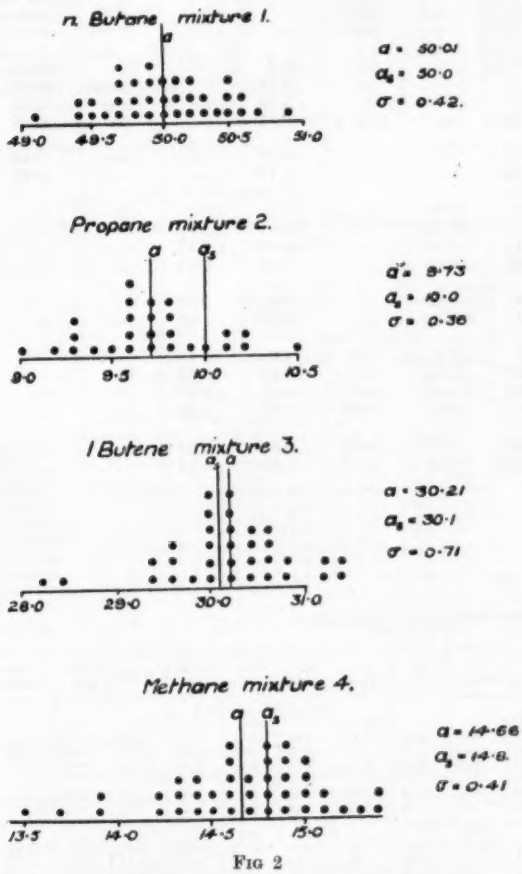

FIG 2

SOME TYPICAL DISTRIBUTIONS

was calculated. The difference between the average analysis obtained for a particular component on each instrument and the synthetic composition was calculated, and d_i for that component was taken as the average of these values without regard to sign.

$$d_i = \frac{\Sigma|a_g - a_s|}{n_g}$$

where a_g is the average value of a group of analyses taken on an instrument over a period of one or two days; n_g is the number of groups. For this calculation, analyses obtained with the same instrument at widely different times were treated as though they were obtained on different instruments.

Finally, in order to obtain a measure of the consistency of analysis on a single instrument over a period of one or two days, a standard deviation σ_i was calculated.

$$\sigma_i^2 = \sum_g \sum_b (x_b - a_g)^2/(n - n_g)$$

where x_b is any individual value in a group of values of which a_g is the average, the other terms being defined above. This formula results from the application of the standard statistical method for the analysis of the causes of variation, such as given by Davies.[4] The values of σ_i^2 obtained are, in fact, nearly equal to the mean square of the standard deviations in each group of readings.

RESULTS

The results obtained from both methods of computation are shown in Tables III and IV respectively. For the special method the values of d σ, d_i, and σ_i on each component have been averaged over all mixtures without regard to sign and are given in Table V. Two sets of averaged values are given in Table VI for the general method, according to whether the component was present in or absent from the mixtures.

In connexion with the results shown in Table IV the following points should be noted:

(i) The values for carbon dioxide were based on only five measurements. No value of d_i and σ_i was calculated, and the component was not included in Table VI.

(ii) The values obtained for nitrogen in mixture 4 may not be truly representative of the accuracy that can be obtained on this component in this mixture. Four samples became contaminated with large amounts of air. Air was determined as one component on the 32 peak, and nitrogen was taken as residual 28. However, this method of correcting the 28 peak for the nitrogen of the air may have been faulty, since high values were reported for nitrogen in these four samples. Excluding these four doubtful values, the average of the remaining seventeen is 0·33 mole per cent, with a standard deviation of 0·71 mole per cent. The results on this component in mixture 4 were neglected in computing the average values for nitrogen in Table VI.

(iii) In view of the accuracy obtained on propane in mixtures 2, 3, and 4 the average analysis of +1·02 mole per cent for propane in mixture 1 is taken as indicating the presence of a small quantity of propane impurity in mixture 1. The values of d, σ, d_i, and σ_i obtained on this component in mixture 1 were not included in the average values for propane given in Table VI.

TABLE III

Analyses Computed by the Special Method of Computation

	Methane	Ethane	Propane	Propene	*n*-Butane	*iso*-Butane	1-Butene	*trans*-2-Butene	*iso*-Butene
Mixture 1 (36 determinations):									
Synthetic composition, a_s	—	—	—	—	50·0	—	—	50·0	—
Average analysis, a	—	—	—	—	50·01	—	—	49·99	—
$a - a_s = d$	—	—	—	—	+0·01	—	—	−0·01	—
Standard deviation, σ	—	—	—	—	0·42	—	—	0·42	—
For single instruments:									
Average difference, d_i	—	—	—	—	0·33	—	—	0·33	—
Standard deviation, σ_i	—	—	—	—	0·26	—	—	0·26	—
Mixture 2 (27 determinations):									
Synthetic composition, a_s	—	—	10·0	—	—	29·9	—	—	60·1
Average analysis, a	—	—	9·73	—	—	29·93	—	—	60·32
$a - a_s = d$	—	—	−0·27	—	—	+0·03	—	—	+0·22
Standard deviation, σ	—	—	0·36	—	—	0·33	—	—	0·49
For single instruments:									
Average difference, d_i	—	—	0·32	—	—	0·30	—	—	0·46
Standard deviation, σ_i	—	—	0·20	—	—	0·17	—	—	0·27
Mixture 3 (34 determinations):									
Synthetic composition, a_s	—	—	20·0	20·0	—	29·9	30·1	—	—
Average analysis, a	—	—	19·87	20·02	—	29·92	30·21	—	—
$a - a_s = d$	—	—	−0·13	+0·02	—	+0·02	+0·11	—	—
Standard deviation, σ	—	—	0·64	0·95	—	0·78	0·71	—	—
For single instruments:									
Average difference, d_i	—	—	0·47	0·68	—	0·62	0·52	—	—
Standard deviation, σ_i	—	—	0·15	0·24	—	0·25	0·20	—	—
Mixture 4 (43 determinations):									
Synthetic composition, a_s	14·8	20·0	15·2	15·1	9·9	9·9	15·1	—	—
Average analysis, a	14·66	19·92	14·92	15·23	9·78	10·17	15·23	—	—
$a - a_s = d$	−0·14	−0·08	−0·28	+0·13	−0·12	+0·27	+0·13	—	—
Standard deviation, σ	0·41	0·66	0·50	0·38	0·29	0·40	0·39	—	—
For single instruments:									
Average difference, d_i	0·39	0·49	0·37	0·32	0·23	0·39	0·30	—	—
Standard deviation, σ_i	0·18	0·14	0·20	0·16	0·18	0·18	0·16	—	—

TABLE IV

Analyses Computed by the General Method of Computation

	Methane	Ethane	Ethylene	Propane	Propene	*n*-Butane	*iso*-Butane	1-Butene	2-Butenes	*iso*-Butene	Total butenes	Hydrogen	Oxygen	Nitrogen	Carbon dioxide
Mixture 1 (18 determinations):															
Synthetic composition, a_s	—	—	—	—	—	50·0	—	—	50·0	—	50·0	—	—	—	—
Average analysis, a	−0·07	−0·13	−0·56	1·02	0·01	49·32	0·00	4·52	49·18	−3·93	49·77	−0·02	0·14	0·66	0·14
$a - a_s = d$	−0·07	−0·13	−0·56	+1·02	+0·01	−0·68	0·00	+4·52	−0·82	−3·93	−0·23	−0·02	+0·14	+0·66	+0·14
Standard deviation, σ	0·12	0·16	0·66	0·67	0·18	1·40	0·62	5·32	1·70	4·29	0·64	0·07	0·26	0·87	0·12
For single instruments:															
Average difference, d_i	0·10	0·12	0·52	1·12	0·14	1·26	0·51	3·91	1·62	3·02	0·46	0·06	0·26	0·96	—
Standard deviation, σ_i	0·02	0·05	0·29	0·14	0·10	0·41	0·21	0·99	0·79	0·49	0·37	0·04	0·11	0·42	—
Mixture 2 (17 determinations):															
Synthetic composition, a_s	—	—	—	10·0	—	—	29·9	—	—	60·1	60·1	—	—	—	—
Average analysis, a	−0·07	0·01	−0·14	9·75	0·16	−0·16	30·06	2·85	−1·62	58·88	60·10	0·01	0·11	0·14	0·12
$a - a_s = d$	−0·07	+0·01	−0·14	−0·25	+0·16	−0·16	+0·16	+2·85	−1·62	−1·22	0·00	+0·01	+0·11	+0·14	+0·12
Standard deviation, σ	0·09	0·09	0·35	0·48	0·36	0·34	0·42	7·80	6·32	3·66	0·78	0·07	0·17	0·74	0·12
For single instruments:															
Average difference, d_i	0·07	0·06	0·20	0·35	0·27	0·30	0·43	3·12	2·87	1·70	0·52	0·04	0·12	0·33	—
Standard deviation, σ_i	0·04	0·05	0·29	0·25	0·20	0·13	0·24	4·91	1·84	2·95	0·64	0·06	0·15	0·66	—
Mixture 3 (20 determinations):															
Synthetic composition, a_s	—	—	—	20·0	20·0	—	29·9	30·1	—	—	30·1	—	—	—	—
Average analysis, a	−0·10	0·06	−0·12	19·90	20·46	−0·19	29·78	30·08	0·12	−0·22	29·98	0·01	0·07	0·15	0·15
$a - a_s = d$	−0·10	+0·06	−0·12	−0·10	+0·46	−0·19	−0·12	−0·02	+0·12	−0·22	−0·12	+0·01	+0·07	+0·15	+0·15
Standard deviation, σ	0·14	0·09	0·30	0·73	0·51	0·38	0·79	2·88	2·47	1·28	0·95	0·09	0·07	0·68	0·16
For single instruments:															
Average difference, d_i	0·13	0·17	0·25	0·61	0·45	0·37	0·59	2·27	1·80	0·95	0·83	0·07	0·04	0·54	—
Standard deviation, σ_i	0·03	0·04	0·18	0·17	0·25	0·10	0·37	2·01	1·83	0·91	0·26	0·07	0·06	0·38	—
Mixture 4 (21 determinations):															
Synthetic composition, a_s	14·8	20·0	—	15·2	15·1	9·9	9·9	15·1	—	—	15·1	—	—	—	—
Average analysis, a	14·31	19·91	0·38	14·52	15·01	9·47	9·93	15·76	−0·86	0·02	14·92	0·17	0·09	1·21	0·03
$a - a_s = d$	−0·49	−0·09	+0·38	−0·68	−0·09	−0·43	+0·03	+0·66	−0·86	+0·02	−0·18	+0·17	+0·09	+1·21	+0·03
Standard deviation, σ	0·65	0·74	0·70	0·75	0·45	0·43	0·43	2·30	1·75	0·84	0·74	0·21	0·08	1·91	0·06
For single instruments:															
Average difference, d_i	0·59	0·44	0·46	0·68	0·53	0·47	0·30	1·08	1·03	0·37	0·47	0·21	0·10	1·38	—
Standard deviation, σ_i	0·26	0·34	0·44	0·33	0·23	0·18	0·16	0·51	0·56	0·51	0·24	0·15	0·06	0·72	—

TABLE V

Summary of the Analyses Computed by the Special Method of Computation

Component	Concentration range, mole %	Average values, mole %			
		d	σ	d_i	σ_i
Methane	15	0·1	0·4	0·4	0·2
Ethane	20	0·1	0·7	0·5	0·2
Propane	10–20	0·2	0·5	0·4	0·2
Propene	15–20	0·1	0·7	0·5	0·2
n-Butane	10–50	0·1	0·4	0·3	0·2
*iso*Butane	10–30	0·1	0·5	0·4	0·2
1-Butene	15–30	0·1	0·6	0·4	0·2
trans-2-Butene	50	0·0	0·4	0·3	0·3
*iso*Butene	60	0·2	0·5	0·5	0·3
Average (over all components and all mixtures)	—	0·12	0·51	0·40	0·20

TABLE VI

Summary of the Analyses Computed by the General Method of Computation

Component	Concentration range, mole %	The component present in the mixture				The component absent from the mixture			
		Average values, mole %				Average values, mole %			
		d	σ	d_i	σ_i	d	σ	d_i	σ_i
Methane	15	0·5	0·7	0·6	0·3	0·1	0·1	0·1	0·03
Ethane	20	0·1	0·7	0·4	0·3	0·1	0·1	0·1	0·05
Ethylene	—	—	—	—	—	0·3	0·5	0·4	0·3
Propane	10–20	0·3	0·7	0·6	0·3	—	—	—	—
Propene	15–20	0·3	0·5	0·4	0·2	0·1	0·3	0·2	0·1
n-Butane	10–50	0·6	0·9	0·8	0·3	0·2	0·4	0·3	0·1
*iso*Butane	10–30	0·1	0·6	0·3	0·3	0·0	0·6	0·5	0·2
1-Butene	15–30	0·3	2·6	1·7	1·5	3·7	6·6	3·5	3·0
2-Butenes	50	0·8	1·7	1·6	0·8	0·9	3·5	1·9	1·4
*iso*Butene	60	1·2	3·7	1·7	3·0	1·4	2·9	1·5	0·6
Total butenes	15–60	0·1	0·8	0·6	0·4	—	—	—	—
Hydrogen	—	—	—	—	—	0·05	0·1	0·1	0·08
Oxygen	—	—	—	—	—	0·1	0·2	0·15	0·1
Nitrogen	—	—	—	—	—	0·3	0·8	0·6	0·5

DISCUSSION

Special Method

For each of the components listed in Table III, the parameters d and σ when taken together indicate that there is little systematic error in the mass spectrometric method, taken as a whole. The composition of the mixtures was known only to the nearest 0·1 mole per cent compared with the mean difference of 0·12 mole per cent. However, the average error to be expected in practice in the analysis of a C_1–C_4 sample on a single instrument, as measured by the average value of d_i, is 0·40 mole per cent. This is not surprising in view of the many factors which affect the final accuracy of an analysis. Much of the error of 0·40 mole per cent arises through the collective effect of small random errors in cracking patterns, relative sensitivities, and in the measurement of mixture peak height, though it is possible that some may also occur as a result of a genuine systematic error in the instrument concerned.

The repeatability of analysis on a single instrument was very good. The low value of the standard deviation, σ_i, 0·20 mole per cent, compared with 0·40 mole per cent for d_i, shows that there is little to be gained in accuracy by carrying out several repeat runs of the same sample on a single instrument. (This was also true of the components determined in the general method with the exception of the butene separation, which is improved with repeat determinations.)

The average values of the four parameters d, σ, d_i, and σ_i in Table VII give a simple overall picture of the results obtained in this co-operative programme. It

TABLE VII

The Accuracy of Analysis on the Sector Type Mass Spectrometer

	Special method	General method * for components present in mixtures
Average difference per component between the average analysis and the synthetic composition, d	0·12	0·26
Average standard deviation, σ	0·51	0·68
Average accuracy of analysis of a C_1–C_4 sample on a single instrument, d_i	0·40	0·55
Average standard deviation on a single instrument (over a period of one or two days), σ_i	0·20	0·29

* Omitting individual butenes and taking the total butene values.

is seen that in the general method of computation the accuracy of analysis on those hydrocarbons known to be present in the blends was decreased, but not markedly so.

General Method

From the results obtained by the general method of computation (Table IV), it is seen that small spurious values may be obtained for the concentrations of components not present in a sample. The magnitude of this error varies considerably with the component, and is critically dependent on the nature of its cracking pattern. The components have been classified according to cracking pattern under four main groups in Table VIII, and the values that are likely to be obtained for the concentration of these components in the analysis of a C_1–C_4 sample on a single instrument, when the sample is completely free of these gases, are also given in this table. This quantity has been estimated by taking the average value of d_i for the appropriate components in Table IV.

Though it was found difficult to separate the butene isomers, the total butene content of each mixture was accurately estimated (see Table IV).

It should be emphasized that the values given in Table VIII do not represent the ultimate limit of accuracy of the mass spectrometer in the determination of any component. The figures indicate the

errors to be expected when the sample is treated as a routine C_1–C_4 sample and no special precautions taken to detect impurities.

TABLE VIII

Spurious Values Likely to Occur in the Analysis of a C_1–C_4 Sample on a Single Instrument

Group	Components	Average value of d_i mole per cent	Nature of the cracking pattern
1	Methane, ethane, hydrogen, oxygen	0·10	Cracking patterns contain a peak which is either unique or very nearly so.
2	*n*-Butane, *iso*butane, propene	0·32	No unique peak, but the components are determined from well-conditioned equations.
3	Ethylene, nitrogen	0·48 *	The components are determined from the 26, 27, 28 peaks, to which other hydrocarbons contribute to a great extent.
4	1-Butene, 2-butenes, *iso*butene	2·16	The cracking patterns are very similar.

* The value for nitrogen in mixture 4 has been omitted in computing this verage (see section on results).

Comparison with Work Reported by Starr and Lane

It is interesting to compare the results obtained in this programme with those of Starr and Lane,[2] who reported the results of a co-operative analysis programme carried out entirely on 180° mass spectrometers. One difficulty in making this comparison is that it is not known what computing method was used by Starr and Lane. Examination of their data suggests that their results should be compared with those obtained in the special method in this work, since small values of the type shown in Table IV were not reported by Starr and Lane. These authors also treat their results rather differently, in that probable error is used as a criterion of precision instead of standard deviation and that a few of the worst analyses are rejected through the application of the Chauvenet criterion. Therefore, in order to provide a common basis of comparison, the results have been modified as follows :

(*a*) The same criterion of rejection as used by Starr and Lane was applied to the results obtained in the special method of computation in this programme.

(*b*) The figures given by Starr and Lane for the probable errors have been divided by 0·6745 in order to obtain standard deviations.

The results of the two programmes are compared in Table IX. The values of the average difference, d, and the average standard deviation, quoted for each component, have been obtained by averaging over all mixtures without regard to sign. Though the two programmes differed in the total number of analyses and in the components analysed, it is thought that the figures given in Table IX are sufficiently representative to allow a fair comparison to be made. The figures indicate that the analytical errors in the two programmes were about the same.

TABLE IX

The Comparison of the Results of this Programme with those Reported by Starr and Lane

Component	This programme (after application of the Chauvenet criterion)				Starr and Lane			
	No. of runs	Concentration range, mole %	Av. diff. d, mole %	Av. standard deviation, mole %	No. of runs	Concentration range, mole %	Av. diff. d, mole %	Av. standard deviation, mole %
Methane	41	15	0·1	0·4	—	—	—	—
Ethane	40	20	0·2	0·4	—	—	—	—
Propane	97	10–20	0·2	0·4	124	0·7–10	0·2	0·3
Propene	75	15–20	0·1	0·6	74	7–16	0·6	0·8
n-Butane	78	10–50	0·1	0·3	251	1–84	0·2	0·4
*iso*Butane	96	10–30	0·1	0·4	253	0–45	0·3	0·5
Butene	135	15–60	0·2	0·4	238	9–99	0·2	0·5
Butadiene	—	—	—	—	131	0·2–86	0·1	0·4
n-Pentane	—	—	—	—	98	0–95	0·1	0·4
*iso*Pentane	—	—	—	—	107	0·3–18	0·2	0·3
Average	562	—	0·14	0·42	1276	—	0·22	0·42

ACKNOWLEDGMENTS

This work was made possible by the active support and co-operation of many persons, and the authors gratefully acknowledge the help given by the managements and the staffs of the co-operating laboratories and by the members of the Mass Spectrometry Panel. They also wish to thank Miss W. D. Hall, who made many of the final calculations, and the Royal Dutch–Shell Group for preparing the blends. Permission for the authors' own contribution—the co-ordination of the results—was given by B. G. Churcher, manager, Research Department, and Dr C. Dannatt, Director of Research, Metropolitan-Vickers Electrical Co. Ltd.

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[2] Starr, C. E., and Lane, T. *Anal. Chem.*, 1949, **21**, 572.
[3] *see* Shepherd, M. *Bur. Stand. J. Res., Wash.*, 1947, **19**, 635 and the references there cited.
[4] O. L. Davies. "Statistical methods in research and production," London : Oliver and Boyd, 1949. Chapter V.

ALKYLNAPHTHALENES

PART X. 1:4-DIMETHYLNAPHTHALENE AND SOME TRIALKYLNAPHTHALENES*

By R. F. EVANS, J. C. SMITH (FELLOW), and F. B. STRAUSS

SUMMARY

In this group of hydrocarbons another of the five liquid dimethylnaphthalenes, 1 : 4-dimethylnaphthalene, has been carefully prepared and purified; its physical constants and spectra (ultra-violet and infra-red) are recorded. From the two tetralones, 1 : 3- and 1 : 4-dimethyl-5-keto-5 : 6 : 7 : 8-tetrahydronaphthalene, the corresponding trimethyl- and dimethylethyl-naphthalenes have been prepared in small quantity; the spectra are recorded, and a series of molecular complexes with picric acid, etc, are described.

1 : 4-DIMETHYLNAPHTHALENE

THIS dimethylnaphthalene is first noted in the literature as a product of the distillation with zinc dust of santonin and its derivatives.[1] It is also produced in the zinc-dust distillation of certain fruit juices.[2]

Early syntheses included treatment of 1 : 4-dibromonaphthalene with methyl iodide and sodium in toluene,[3] and the elimination of the amino-group from 1 : 4-dimethyl-2-aminonaphthalene.[4] Meyer and Fricke [5] passed a mixture of acetylene, methane, and hydrogen over a heated catalyst and isolated 1 : 4-dimethylnaphthalene from the mixture of products. These preparations of the hydrocarbon all appeared to yield specimens liquid down to −20°.

In the early 1930s the hydrocarbon was obtained from dimethyl sulphate and the lithium derivative of 4-bromo-1-methylnaphthalene, and was reported to melt at 15° to 17°.[6] Robinson and Thompson,[7] however, obtained from the action of dimethyl sulphate on 4-bromo-1-methylnaphthalene a product which, after several crystallizations from alcohol, melted at 5·5° to 6·5°. Darzens [8, 9] and Bailey *et al* [10] chloromethylated 1-methylnaphthalene and reduced the 1-methyl-4-chloromethylnaphthalene so obtained; the melting point of the liquid product recorded by Bailey *et al* was 5° to 6°.

Kloetzel [11] dehydrogenated the dimethyldihydronaphthalene obtained by the reaction between methylmagnesium iodide and 4-methyl-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. Barnett and Sanders [12] used the obviously direct and unambiguous route by subjecting *p*-xylene to the succinic anhydride synthesis.

For this synthesis pure *p*-xylene of f.p. 13·27° was prepared from commercial xylene.

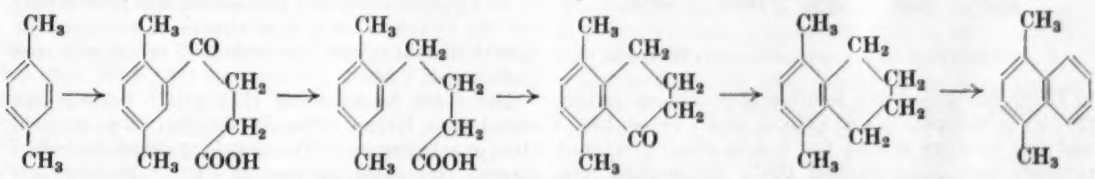
EXPERIMENTAL

p-Xylene. 5·5 litres of commercial mixed xylenes, in 250-cc portions, were cooled with stirring to −65° and the solid was collected. On melting this gave 1026 cc of n_D^{20} 1·4937; it was refluxed 8 hr with aqueous mercuric acetate solution (in order to remove sulphur compounds), the mixture cooled and the hydrocarbon layer dried. On distillation through a Stedman column it gave a main fraction (823 cc of b.p. 135° to 137°, m.p. 5·5°) which was crystallized at 0° from ethanol. Thus were obtained 320 cc with the following constants :

	Present specimen	Bureau of Standards [13]
F.p. . . .	13·27°	13·263°
B.p. . . .	137·8°/756 mm	138·348°/760 mm
n_D^{20} . . .	1·4959	1·49581
D_4^{20} . . .	0·8609	0·86105

The freezing curve in the Rossini apparatus [14] showed no measurable drop from the maximum temperature during 60 min, and the purity of the sample appears to be well over 99·9 per cent.

Several attempts were made to prepare *p*-xylene from toluene by the chloromethylation process. Most of the modifications tried gave a yield of 20 to 40 per cent of crude ω-chloroxylenes (chloromethyltoluenes), b.p. 110° to 120°/40 mm. Reduction of this mixture with zinc dust and dil sodium hydroxide solution gave products of b.p. 135° to



* MS received 28 May 1953.

150°/760 mm and n_D^{20} 1·4995. Assuming a linear relationship between n_D^{20} and the composition of an *o*- and *p*-xylene mixture, the distillate contained 38·5 per cent of *o*-xylene. Hill and Short [15] by freezing-point methods found that a similar mixture yielded 41·7 per cent of *o*-xylyl and 58·3 per cent of *p*-xylyl alcohol.

Since this work was carried out, an interesting method of preparing *p*-xylene from toluene *via* *p*-tolylsodium has been described by Bryce-Smith and Turner.[16]

β-2 : 5-*Dimethylbenzoylpropionic acid*. Powdered aluminium chloride (401 g, 3 mol) was added gradually with swirling to a mixture of succinic anhydride (150 g, 1·5 mol) pure *p*-xylene (195 cc, 1·58 mol) and redistilled tetrachloroethane (600 cc). After standing for 48 hr the mixture yielded 285 g (93 per cent) of impure keto-acid. Further experiments, each on 0·74 mol scale, gave 93 and 98 per cent yields respectively. Crystallization from benzene gave acid of m.p. 85·5° to 86·3°. M.p.s recorded in the literature are 62°,[17] 80°,[18] 81° to 82°,[19] 84°,[20] and 86°.[12]

γ-2 : 5-*Dimethylphenylbutyric Acid*. Clemmensen reductions of the keto-acid on a 100-g scale gave quantitative yields. The product, crystallized from benzene, melted at 71° to 72·5°. Barnett and Sanders [12] give m.p. 70°.

1 : 4-*Dimethyl-5-keto-5* : 6 : 7 : 8-*tetrahydronaphthalene*. The above described acid (82·5 g, m.p. 71° to 72·5°) was added to a solution of phosphoric oxide (247 g) in phosphoric acid (275 cc of *d* 1·75) at 165°, and the mixture stirred for 3 min after the temperature had again reached 165°. On working up by pouring into water and extracting with ether the mixture gave 69·4 g (93 per cent) of tetralone b.p. 132°/0·05 mm which solidified. Crystallization from light petroleum gave large plates of m.p. 31·5°. Barnett and Sanders [12] appear to be the only authors who have previously obtained this tetralone as a solid. They give the m.p. as 33°.

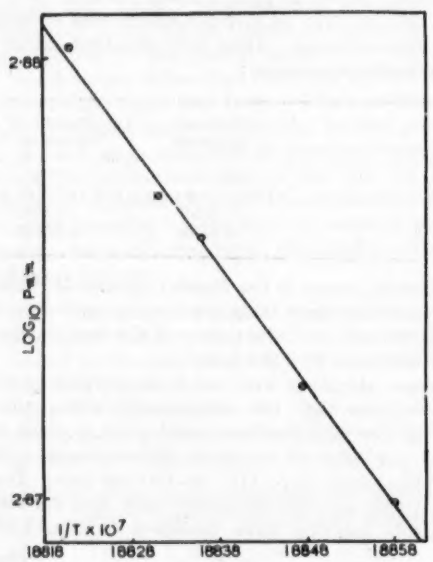


Fig 1

1 : 4-DIMETHYL-5 : 6 : 7 : 8-TETRAHYDRONAPHTHALENE

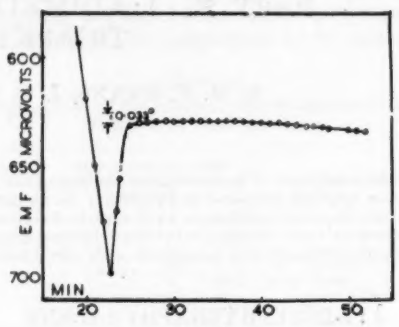


Fig 2

1 : 4-DIMETHYL-5 : 6 : 7 : 8-TETRAHYDRONAPHTHALENE

[The residue from distillation of the tetralone was crystallized five times from ethanol–benzene and yielded a white solid, m.p. 222·5°, which decolorized alkaline permanganate.]

The *oxime* of the tetralone crystallized from light petroleum in prisms of m.p. 145·5°. [Found: C, 76·5; H, 8·0 per cent. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0 per cent.] A red 2 : 4-*dinitrophenylhydrazone* crystallized from benzene and melted at 252° to 254° (decomp). [Found: C, 61·2; H, 4·9 per cent. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1 per cent.]

1 : 4-*Dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*. By Huang-Minlon reduction the tetralone (184·5 g) gave 158·5 g (93 per cent yield) of colourless hydrocarbon, b.p. 134° to 138°/17 mm. The small quantity of residue, on crystallization from ethanolic benzene, formed golden-yellow prisms of m.p. 162·5°. [Found: C, 83·7; H, 8·0 per cent. The *azine*, $C_{24}H_{28}N_2$, requires C, 83·7; H, 8·2 per cent.] On fractionation under reduced pressure this tetralin gave a large constant-boiling fraction which was examined in the Rossini [14] apparatus. It had f.p. −4·13°, which, corrected to zero impurity, reached −4·0°. The b.p. was 258·2°/760 mm; n_D^{20} 1·5471; d_4^{20} 0·9738; hence $[R_L]_D^{20}$ was 52·20 and exaltation, 0·38. (Figs 1 and 2.)

1 : 4-*Dimethylnaphthalene*. By refluxing the tetralin with palladized charcoal (10 per cent Pd), in the ratio of 13 g hydrocarbon to 1 g charcoal, and by sweeping out the hydrogen in a slow stream of nitrogen, the dimethylnaphthalene was obtained in 96 per cent yield within 5 hr.

The crude hydrocarbon (114 g, n_D^{20} 1·6090) was added to a boiling ethanolic solution of picric acid (158 g in 1200 cc). The orange precipitate, when filtered and dried, melted at 143°. (Barnett and Sanders [12] give m.p. 144°.) [Found: C, 56·4; H,

4·2 per cent. Calc for $C_{18}H_{15}O_7N_3$, C, 56·1; H, 3·9 per cent.] From the mother liquor impure hydrocarbon of n_D^{20} 1·5800 was obtained. As this obviously contained the tetrahydronaphthalene, it was again refluxed with palladized charcoal and the

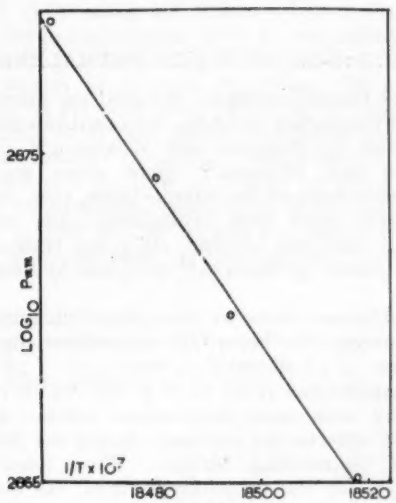


FIG 3

1 : 4-DIMETHYLNAPHTHALENE

product converted into picrate, m.p. 143° to 144° (uncorr).

The combined picrate preparations (258 g), decomposed with dilute sodium hydroxide solution in presence of light petroleum, b.p. 60° to 80°, gave 101 g (88 per cent recovery) of dimethylnaphthalene, b.p. 140° to 144°/19 mm, n_D^{20} 1·6140. After repeated fractional distillation under reduced pressure the

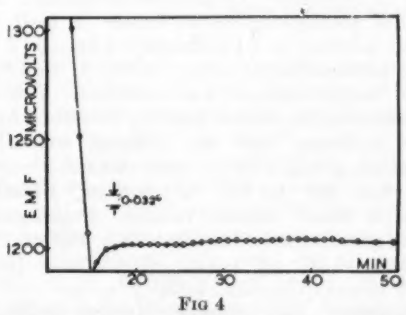


FIG 4

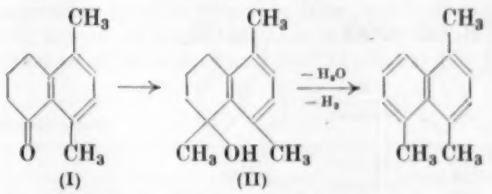
1 : 4-DIMETHYLNAPHTHALENE FREEZING CURVE

large constant-boiling fraction was examined: the b.p. was 268·8°/760 mm, and f.p. 7·85°. Extrapolation to zero impurity [14] gave f.p. 7·87°. Other constants were n_D^{20} 1·6141, d_4^{20} 1·0168; $[R_L]_D^{20}$ was 53·56, with exaltation, 2·68. The pure hydrocarbon gave an orange picrate of m.p. 143° to 144°, a golden styphnate of m.p. 126° to 127°, and a yellow *symtrinitrobenzene* complex of m.p. 165° to 166° (or 167·5° to 168·5° corr). (Figs 3 and 4.)

1 : 4 : 5-TRIMETHYLNAPHTHALENE

Two syntheses of this hydrocarbon have already been reported. Barnett and Sanders [12] proceeded through the succinoylation of *p*-xylene; Ruzicka and Ehmann [22] used acetyl *p*-xylene (2 : 5-dimethylacetophenone) in the Reformatsky reaction and built up the required *γ*-2 : 5-dimethylphenylvaleric acid. Both routes led to a trimethylnaphthalene of m.p. 63°.

In this investigation Barnett's synthesis was repeated and a final product of m.p. 62° was obtained.



In the dehydration of the methyltetralol II, even with copper sulphate, a large amount of dimolecular by-product was obtained. The crude trimethylnaphthalene was purified through the picrate. A trinitrobenzene complex was also prepared.

EXPERIMENTAL

1 : 4 : 5-*Trimethyl*-7 : 8-*dihydronaphthalene*. 1 : 4-Dimethyl-5-keto-5 : 6 : 7 : 8-tetrahydronaphthalene (see p. 8, 34·8 g, 1 mol) in ether (174 cc) was added to the stirred ice-cold Grignard solution (2 mol, prepared from 9·6 g of magnesium, 57 g of methyl iodide, and 150 cc of ether). After having stood 12 hr the mixture was decomposed with ammonium chloride solution and gave 47·4 g (100 per cent) of a yellow-green, solid, methyltetralol. When this product was heated at 100° for 3 hr with anhydrous copper sulphate it gave only 22·2 g (64 per cent) of a fraction b.p. 170° to 200°/56 mm, n_D^{20} 1·5712. A residue failed to distil.

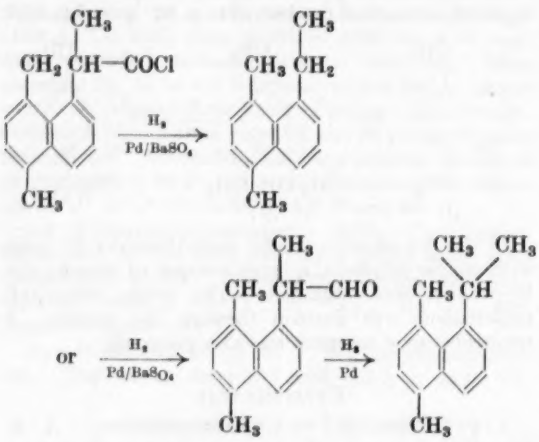
1 : 4 : 5-*Trimethylnaphthalene*. The dihydronaphthalene (21·6 g), refluxed 5 hr with palladized charcoal (4 g of 10 per cent Pd), gave 18 g (84 per cent) of crude trimethylnaphthalene, b.p. 180° to 190°/45 mm, m.p. 52°. This solid, in ethanol (45 cc), was added to a hot solution of picric acid (23 g in 80 cc of ethanol). From the resulting picrate (28 g of orange needles, m.p. 143° to 144·5°) the hydrocarbon was regenerated and then distilled, giving 11·8 g of m.p. 53°. After 4 crystallizations from ethanol a product of f.p. and m.p. 61·8° was obtained; in a capillary tube it melted at 61·5° to 62°. (Literature 63°.[12, 22])

Reconversion to the picrate gave deep orange needles which, crystallized from ethanol, melted at 144° to 145°. [Found: C, 57·25; H, 4·1 per cent. Calc for $C_{19}H_{17}O_7N_3$: C, 57·1; H, 4·4 per cent.] Ruzicka [22] gives m.p. 144° to 145°; Barnett [12] gives 146°. The *trinitrobenzene complex*, golden rods from ethanol,

melted at 162° to 163·5°. [Found: N, 10·9 per cent. $C_{19}H_{17}O_6N_3$ requires N, 11·0 per cent.]

1 : 4-DIMETHYL-5-ETHYLNAPHTHALENE

Newman and Hussey [23] obtained a liquid hydrocarbon of n_D^{25} 1·6108 when they reduced α-(1 : 4-dimethyl-5-naphthyl)propionyl chloride with hydrogen at 160° to 170° in presence of palladized barium sulphate. They assumed the loss of carbon monoxide and formation of 1 : 4-dimethyl-5-ethylnaphthalene, instead of the required aldehyde.



The hydrocarbon made here by the same route as was 1 : 4 : 5-trimethylnaphthalene had a lower refractive index than that of Newman's hydrocarbon, which may well have been 1 : 4-dimethyl-5-*iso*propylnaphthalene. (Little detail was given by Newman and Hussey.)

Experimental

1 : 4-*Dimethyl-5-ethyl-7 : 8-dihydronaphthalene*. 1 : 4-Dimethyl-5-keto-5 : 6 : 7 : 8-tetrahydronaphthalene (45·5 g, 1 mol) in ether (230 cc) was added to a vigorously stirred, ice-cold Grignard solution (2 mol) obtained from magnesium (12·7 g), ethyl bromide (57·8 g), and ether (100 cc). The mixture remained 2 hr at 0° and was then refluxed 3 hr. The product, heated at 100° for 2 hr with anhydrous copper sulphate (25 g), gave 37·5 g (77 per cent yield, calculated on the tetralone) of the dihydronaphthalene, b.p. 166° to 176°/40 mm.

1 : 4-*Dimethyl-5-ethylnaphthalene* (16·2 g, 82 per cent, n_D^{20} 1·6095) was obtained on refluxing the dihydronaphthalene (20 g) for 5 hr with palladized charcoal (1·5 g of 10 per cent Pd) and extraction of the mixture with ether, filtration, and distillation. Purified through the picrate and (after regeneration) heated with sodium metal at 150°, the liquid hydrocarbon had m.p. −8°, b.p. 154° to 156°/15 mm; n_D^{20} 1·6089; d_4^{20} 1·0113; $[R_L]_D^{20}$ 63·07 and exaltation, 2·95.

The *picrate*, orange needles from ethanol, melted at 82° to 83°. [Found: N, 10·0 per cent. $C_{20}H_{19}O_7N_3$ requires N, 10·2 per cent.] The sym-*trinitrobenzene complex*, yellow needles from ethanol, melted at 111° to 113°. [Found: N, 10·3 per cent. $C_{20}H_{19}O_6N_3$ requires N, 10·6 per cent.] The styphnate was unstable. (Compare Part III.[24])

1 : 3 : 5-TRIMETHYLNAPHTHALENE

It was thought advisable to repeat the preparation of this hydrocarbon which has been used as a reference compound by Heilbron and Wilkinson,[25] and by Ruzicka and Ehmann.[22] Since those specimens were made some of the intermediates, then reported as liquids, have been crystallized. The melting-point of our final product (46°) lay between the values quoted by Heilbron [25] (47°) and by Ruzicka [22] (43°).

The obvious route to this trimethylnaphthalene was through the beautifully crystalline dimethyltetralone, 1 : 3-dimethyl-5-keto-5 : 6 : 7 : 8-tetrahydronaphthalene (Part VI,[26] p. 84), which reacted smoothly with methylmagnesium iodide. An interesting observation was made during the dehydration of the resulting carbinol. When formic acid was used for the dehydration there was obtained 40 per cent of a syrupy by-product which yielded a crystalline substance of m.p. 138°. Its molecular formula was $C_{26}H_{32}$, *i.e.*, a dimeride of the required trimethyldihydronaphthalene. In contrast, dehydration of the carbinol with anhydrous copper sulphate at 100° gave a 93 per cent yield of the dihydronaphthalene; dehydrogenation with palladized charcoal led to the trimethylnaphthalene, and the usual molecular complexes were prepared and analysed.

Experimental

1 : 3 : 5-*Trimethyl-7 : 8-dihydronaphthalene*. By the action of methylmagnesium iodide (2 mol) on an ethereal solution of 1 : 3-dimethyl-5-keto-5 : 6 : 7 : 8-tetrahydronaphthalene (f.p. 48·8°, 1 mol [26]) the viscous methylcarbinol was obtained. The liquid was warmed on the steam bath 1½ hr with anhydrous copper sulphate, and an ethereal extract was evaporated, giving a 93 per cent yield of a colourless liquid, b.p. 133° to 150°/12 mm, n_D^{20} 1·5690, and leaving a small viscous residue. Fractional distillation gave a middle fraction of b.p. 129° to 139°/10 mm, m.p. −13°, n_D^{20} 1·5692, d_4^{20} 0·9784. $[R_L]_D^{20}$ is thus 57·72 and exaltation, 1·75.

Dehydration with Formic Acid: Isolation of Dimeride. (i) The viscous methylcarbinol was heated with 4 times its weight of 98 per cent formic acid 1½ hr on a water bath. From 15 g of tetralone there were obtained 8·8 g (60 per cent yield of trimethyldihydronaphthalene) and 3·7 g of a high-boiling syrup. (ii) When the carbinol from 40 g of tetralone was kept in contact at 24° to 28° with anhydrous formic acid for 2 hr the mixture yielded 28·2 g (71 per cent) of the dihydronaphthalene. From an

ethereal solution of the syrupy residue a sticky solid was obtained on evaporation; crystallized 4 times from acetone it melted at 137·5° to 138°. [Found: C, 90·6; H, 9·5 per cent; mol. wt. in camphor, 318. $(C_{13}H_{16})_2$ requires C, 90·6; H, 9·4 per cent; mol. wt., 344.]

1 : 3 : 5-*Trimethylnaphthalene.* 1 : 3 : 5-Trimethyl-7 : 8-dihydronaphthalene (54·4 g) was refluxed with palladized charcoal (2·7 g of 20 per cent Pd) in a slow stream of nitrogen for 6 hr. The product (51·2 g, 95 per cent yield) boiled at 147° to 160°/16 mm, froze at 42° and melted completely at 44°. It was precipitated as picrate (from ethanol) and the solid complex, air-dried for 2 days, melted at 139·5°.

The hydrocarbon, regenerated from this picrate, boiled at 150° to 156°/16 mm and melted at 45·4°. Four crystallizations of this trimethylnaphthalene from ethanol raised the m.p. to 46°, and the b.p. was 284·5°/760 mm. It gave the pure picrate as orange-red needles (from ethanol), melting at 139·5° to 140·5° (or at 140·5° to 141·5°, corr). [Found: C, 57·2; H, 4·3 per cent. Calc for $C_{13}H_{14}.C_6H_3O_7N_3$: C, 57·5; H, 4·4 per cent.] M.p.s quoted in the literature are 141° to 142° [25] and 140°.[22] The styphnate, yellow needles from ethanol, melted at 137° (or 138·2°, corr). [Found: C, 54·8; H, 4·3 per cent. Calc for $C_{13}H_{14}.C_6H_3O_8N_3$: C, 54·9; H, 4·1 per cent.] M.p.s in the literature are 138° [25] and 136·5°.[22]

The *trinitrobenzene complex*, orange-red needles from ethanol, melted at 154° to 155°. [Found: C, 60·0; H, 4·65; N, 11·2 per cent. $C_{13}H_{14}.C_6H_3O_6N_3$ requires C, 59·6; N, 4·5; H, 11·0 per cent.]

1 : 3-DIMETHYL-5-ETHYLNAPHTHALENE

The preparation of this hydrocarbon was similar to that of 1 : 3 : 5-trimethylnaphthalene except that ethylmagnesium bromide was used instead of methylmagnesium iodide. For the dehydration of the resulting ethyl tetralol only copper sulphate was used. Although two products might be expected from the dehydration (one with an exocyclic double bond), the boiling point was constant throughout the distillation. Dehydrogenation yielded the dimethylethylnaphthalene as a low-melting solid. Here, as is usual, substitution of ethyl for methyl lowered the melting point.

Experimental

The ethyl tetralol, from 1 : 3-dimethyl-5-keto-5 : 6 : 7 : 8-tetrahydronaphthalene (1 mol) and ethylmagnesium bromide (2 mol) in ether, was dehydrated with anhydrous copper sulphate at 90° to 100° (2 hr) giving an 86 per cent overall yield of a liquid dihydro-

Di- and *Tri-Alkylnaphthalenes*

Alkylnaphthalene	M.p., °C	B.p., °C/mm	n_D^{20}	d_4^{20}	Picrate m.p., °C *	Styphnate m.p., °C *	T.N.B. complex m.p., °C *	Authors' Ref.
1 : 4-Me_2	5–6	263/760	1·6127	—	143	126	165–166	10
	5·5–6·5	118/10	—	—	143–144	—	—	7
	7·87	268·8/760	1·6141	1·0168	143–144	126–127	165–166	Present
1 : 4 : 5-Me_3	63	—	—	—	146	—	—	12
	63	145/12	—	—	144–145	129–130	—	22
	62	185/45	—	—	144–145	129–130	162–163	Present
1 : 4-Me_2-5-Et	−8	154–156/15	1·6089	1·0113	82–83	Unstable	111–113	Present
1 : 3 : 5-Me_3	43	—	—	—	140	136·5	—	22
	47	—	—	—	141–142	138	—	25
	46	284·5/760 156/16	—	—	140	137	154–155	Present
1 : 3-Me_2-5-Et	33	—	1·5974	0·9918	108–109·5	115–116	118–119·5	Present
1 : 4-Dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene	−4·13	258·2/760	1·5471	0·9738	—	—	—	Present

* These m.p.s are all uncorrected for the effect of exposed stem.

dimethylethylnaphthalene, b.p. 149°/9 mm, n_D^{20} 1·5599.

On refluxing for 5 hr with palladized charcoal the dihydronaphthalene gave a crude product of n_D^{20} 1·5920. When this was purified through the picrate (m.p. 109°), and then crystallized from ethanol it melted at 33°. Supercooled, it had d_4^{20} 0·9918; n_D^{25} 1·5954, n_D^{20} 1·5974; $[R_L]_D^{20}$ 63·24; exaltation, 3·12. [Found: C, 91·4; H, 8·5 per cent. $C_{14}H_{16}$ requires C, 91·2; H, 8·7 per cent.] The *picrate*, scarlet needles from ethanol, melted at 108° to 109·5°. [Found: C, 58·4; H, 4·8; N, 10·3 per cent. $C_{14}H_{16}.C_6H_3O_7N_3$ requires C, 58·1; H, 4·6; N, 10·2 per cent.] The *styphnate*, golden-orange needles from ethanol, melted at 115° to 116°. [Found: C, 56·2; H, 4·5; N, 9·6 per cent. $C_{14}H_{16}.C_6H_3O_8N_3$ requires C, 56·0; H, 4·5; N, 9·8 per cent.] The *trinitrobenzene complex*, golden needles from ethanol, melted at 118° to 119·5°. [Found: N, 10·5 per cent. $C_{14}H_{16}.C_6H_3O_6N_3$ requires N, 10·6 per cent.]

SPECTRA

The *ultra-violet spectra* were measured in methanol solutions at cell-lengths of 0·1 and 1·0 cm by means of a Unicam spectrophotometer.

The curves obtained for the trimethyl and the dimethylethyl naphthalenes are closely similar, and the graph for only one of them is shown, together with a list of the exact positions of the absorption maxima of the five compounds. (Fig 11 and Table below.)

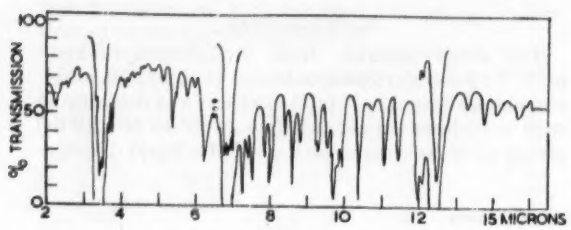


FIG 5

1 : 4-DIMETHYL-5 : 6 : 7 : 8-TETRAHYDRONAPHTHALENE

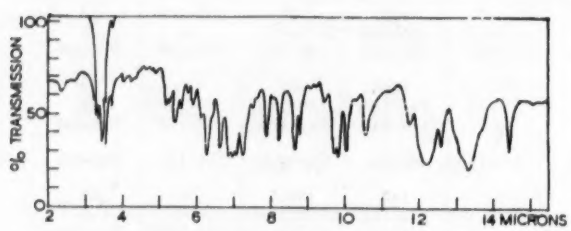


FIG 6

1 : 4-DIMETHYLNAPHTHALENE

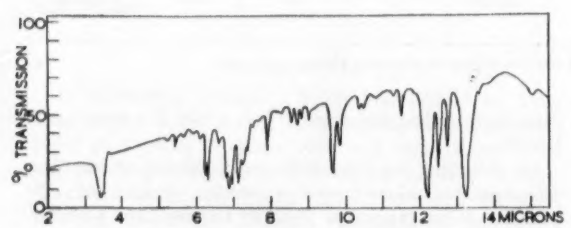


FIG 7

1 : 4 : 5-TRIMETHYLNAPHTHALENE

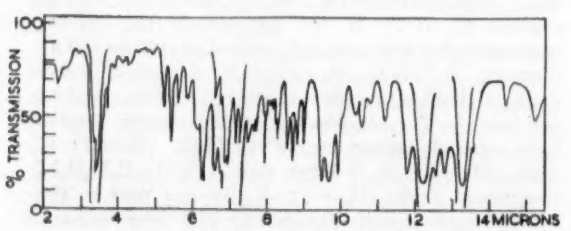


FIG 8

1 : 4-DIMETHYL-5-ETHYLNAPHTHALENE

Absorption Maxima in the Ultra-violet

	Molar $\lambda_{max.}$, Å	Molar $\epsilon_{max.}$	Solvent
1 : 3 : 5-Trimethylnaphthalene	2,300 2,850 3,190 3,248	103,000 7,160 460 510	Methanol
1 : 4 : 5-Trimethylnaphthalene	2,300 2,900 3,200 3,265	100,000 9,500 470 660	Methanol
1 : 3-Dimethyl-5-ethylnaphthalene	2,300 2,900 3,188 3,246	100,000 7,350 500 590	Methanol
1 : 4-Dimethyl-5-ethylnaphthalene	2,300 2,900 3,260	61,400 8,500 970	Methanol
1 : 4-Dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene	2,080 2,170 2,660	11,300 9,400 710	*cyclo*Hexane
1 : 4-Dimethylnaphthalene	2,250 2,900 3,170 3,215	62,500 6,970 630 390	Methanol

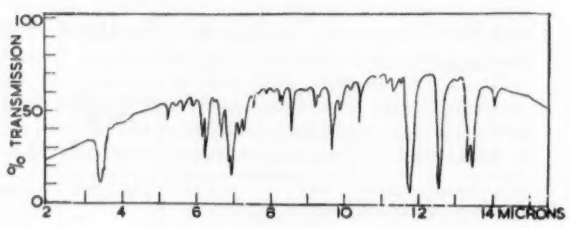


FIG 9

1 : 3 : 5-TRIMETHYLNAPHTHALENE

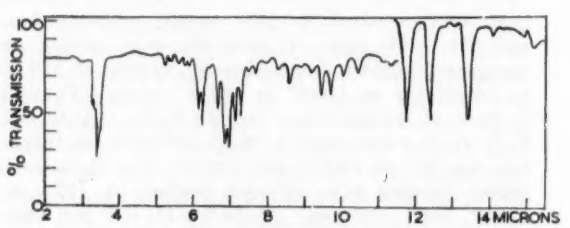


FIG 10

1 : 3-DIMETHYL-5-ETHYLNAPHTHALENE

The spectrum of 1 : 4-dimethyl-5 : 6 : 7 : 8-tetrahydronaphthalene was measured in *cyclo*hexane solution in order to avoid oxidation. No further absorption bands were found in the region above 2800 Å, characteristic for a pure substituted benzene.

The *infra-red spectra* were taken on a Perkin–Elmer Model 21 double-beam instrument fitted with a rock-salt prism. (Figs 5–10.)

1 : 4-Dimethyl-5-ethylnaphthalene, the only one of these compounds which is a liquid at room temperature, was measured in cells of 0·1 and 0·01 cm length. 1 : 3-Dimethyl-5-ethylnaphthalene was measured as a melt, and the two trimethylnaphthalenes as pastes in paraffin.

The two 1 : 4 : 5-substituted compounds obey the known assignment rules for the out-of-plane vibrations of unsubstituted hydrogens of the benzene ring, namely major absorption bands at 12·23 micron

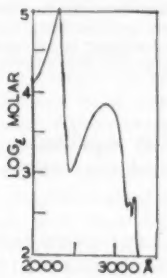


FIG 11

1 : 3 : 5-TRIMETHYLNAPHTHALENE ULTRAVIOLET ABSORPTION SPECTRUM

for the two neighboured hydrogens, and at 13·26 micron for the three neighboured hydrogens.

The 1 : 3 : 5-substituted compounds show similar bands near 12·5 and 13·4 micron, although only the three neighboured hydrogens are present, and the two neighboured hydrogens are absent, while a new band at 11·76 can be correctly assigned to the two un-neighboured hydrogens which are present in these compounds.

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The Dyson Perrins Laboratory,
Oxford University.
May 1953.

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AN EVAPORATION METHOD FOR MEASURING THE RESISTIVITY–WATER SATURATION CHARACTERISTICS OF CORES

By J. BIRKS *

SUMMARY

An evaporation method using a saturated solution of calcium sulphate of constant specific resistance has been developed for measuring the resistivity–water saturation characteristics of cores, and results are presented for typical sandstone and limestone samples. The method can be applied to cores covering the complete range of permeability and porosity; it is rapid and reproducible, and measurements on a large number of cores can be made simultaneously.

INTRODUCTION

In the electric logging of a borehole, now generally considered a routine part of the drilling programme, the resistivity log records the change in apparent resistivity of the structure surrounding the borehole.

Allowing for the effect of the borehole diameter and the mud fluids, the resistivity depends principally on the quantity and salinity of the interstitial water. The salinity can be calculated from the spontaneous potential log or from measurements on oil cut cores. Before the percentage water saturation can be calculated from the resistivity log, and hence by difference the oil or gas saturation, it is necessary to carry out laboratory experiments to determine the resistivity–water saturation relationship.

Various investigators have studied this relationship, and the results of earlier workers gave rise to the following equation [1]:

$$R/R_0 = S^{-n}$$

where S = water saturation, fraction of pore space; R = resistivity of the sand at saturation S; R_0 = resistivity of the sand at 100% saturation.

The saturation exponent n is the factor which is essential for the interpretation of electric logging results, and although a figure of 2·0 is generally accepted, more recent experiments have raised considerable doubt as to the validity of this figure, particularly below water saturation values of 50 per cent.

This paper is, however, concerned primarily with a method of evaluating n for a particular formation and not with the derivation of a relationship between saturation and resistivity index which would have general application, although this aspect of the problem is also being investigated.

To the author's knowledge, three methods of measuring the resistivity–water saturation characteristics of cores have been used in the past. These differ primarily in the method of decreasing the water saturation of the core in a controlled fashion. The main essential is that the water content of the core should be in capillary equilibrium at the time the electrical resistance of the core is measured. The three methods are :—

(1) The capillary pressure technique,[2] in which brine is progressively displaced from the pores by oil or gas, the core being in capillary contact with a porous plate which is permeable to brine, but not to oil or gas. This method finds its most useful application in cores of permeability greater than 50 millidarcies (md), *i.e.*, sandstone cores, since experiments on limestone cores of lower permeability take too long, and require porous plates of high displacement pressure.

(2) Direct measurements on freshly drilled cores using oil as the drilling fluid.[3] This method allows only one measurement to be made on each core, and consequently necessitates a large amount of oil-based coring in order to obtain sufficient experimental data.

(3) An evaporation method using a brine solution.[4] This is a rapid method, but is complicated by the change in specific resistance of the saturating fluid as evaporation proceeds. In addition, it is possible that during evaporation solution equilibrium is not attained and a more concentrated brine may exist at the evaporating surface of the core.

The ideal evaporating liquid would be one of constant composition, good electrical conductivity, and volatility, and of the various mixtures experimented with it was found that a saturated solution of calcium sulphate satisfied these conditions better than any other. This solution has the additional advantages that: (*a*) it does not form supersaturated solutions easily; (*b*) it is present in most formation waters; and (*c*) many limestone rocks contain anhydrite ($CaSO_4$), and its use will prevent the anhydrite from dissolving. The solubility of $CaSO_4$ in water at room temperature is approximately 0·2 per cent, and the effect of the solid $CaSO_4$ precipitated in the pores of a core during evaporation runs can be neglected.

* Anglo-Iranian Oil Co. Ltd.

EXPERIMENTAL METHOD

Small plugs, 1 inch diameter and 1 inch long, used for normal core analysis measurements were used in these experiments. The end faces of the plugs were painted with silver conducting paint * and allowed to dry. The plugs were extracted with distilled water to remove soluble salts from the pores, and where the cores contained anhydrite, the plugs were extracted with a saturated calcium sulphate solution to prevent the anhydrite dissolving. The plugs were dried at 110° C overnight, cooled in a desiccator, and weighed. They were then saturated under vacuum with a saturated solution of calcium sulphate, and left overnight to attain solution and temperature equilibrium in a thermostat at 25° C. The specific resistance of the solution surrounding the cores was compared with that of the original $CaSO_4$ solution. These will be the same if all the soluble salts had been thoroughly extracted from the cores. Each plug in turn was removed from the $CaSO_4$ solution, its surface wiped dry and its resistance measured on an AC conductivity bridge † by making electrical connexion to the two silver-coated surfaces of the plug. It is essential to use short screened leads to the bridge in order to reduce to a minimum stray capacitance which could cause a low apparent resistivity at resistances greater than $\frac{1}{2}$ megohm. This would in fact only effect readings at water saturations of less than 10 per cent of the pore space. After measurements of the resistance, each plug was placed in a weighing bottle and the pore volume of the sample determined from the increase in weight of the plug. The plugs were then allowed to evaporate in a gentle stream of dry air for $\frac{1}{2}$ hour, after which they were placed in separate weighing bottles, and replaced in the thermostat. At least $\frac{1}{4}$ hour was allowed for the plugs to attain temperature and capillary equilibrium (tests over longer times showed that no change in resistivity occurred). The resistance of the plugs and their weights were measured, and another $\frac{1}{2}$-hour period of evaporation started. The percentage pore space saturations of the plugs were calculated from the weights of the cores, and the resistivity ratios R/R_0 from the resistance R of the plug at a particular water saturation and the resistance R_0 of the plug at 100 per cent water saturation.

Half an hour's evaporation is approximately equivalent to a reduction of the water saturation of 10 per cent of the pore space for sandstone cores, and a little less for the low permeability limestone cores. A complete saturation range can be easily covered in 12 hours. It does not affect the results, however, if the plugs are sealed in their weighing bottles, kept in the thermostat overnight, and the evaporation runs continued the next day.

RESULTS

A saturated solution of calcium sulphate contains approximately 0·2 g of $CaSO_4$ per 100 cc of solution at 25° C. Measurements of the specific resistance of the solution showed that it was unchanged with decrease in volume as water was allowed to evaporate, and a precipitate of $CaSO_4$ formed immediately without supersaturation occurring.

Table I lists the characteristics of typical cores studied.

TABLE I

Core	K_a md	Porosities, % pore space				Formation factor, F		
		Air	$CaSO_4$	1% NaCl	5% NaCl	$CaSO_4$	1% NaCl	5% NaCl
Sandstone								
1	208	23·4	20·4	20·3	20·3	13·1	13·7	12·8
2	274	18·5	16·9	17·0	16·9	18·5	19·7	18·3
3	268	18·2	15·2	15·3	15·3	21·8	21·2	20·0
Limestone								
1	902	27·5	26·3	26·2	26·5	13·2	13·9	13·3
2	1·0	16·8	14·7	15·2	14·7	50·8	72·0	72·3
3	0·09	4·6	4·0	4·06	4·05	159	465	560

Fig 1 shows duplicate runs made on a sandstone core. Run 1 was made on the freshly extracted core,

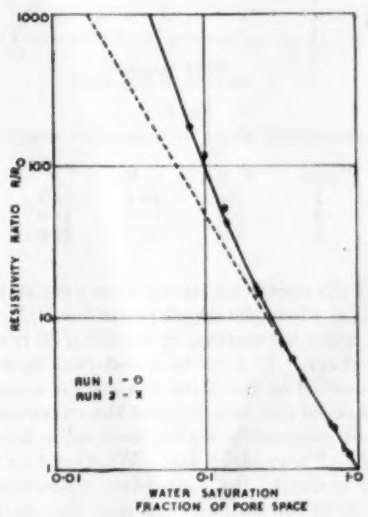

FIG 1

DUPLICATE RUN ON SANDSTONE CORE NO. 3

the stages of evaporation being carried out over two successive days with the plugs left overnight in sealed weighing bottles in the thermostat. Run 2 was made after resaturating the dried cores from Run 1 (*i.e.*, with solid $CaSO_4$ left in the pores) and was carried out over a continuous 12-hour period. The good agreement obtained in duplicate runs on all the plugs studied showed that no supersaturation of the $CaSO_4$ solution occurred during evaporation (since in the second runs solid $CaSO_4$ was always present), and that capillary equilibrium existed at the time of measurement of resistivities.

* Elargol W.4 (Ward, Blenkinsop & Co. Ltd., London). † Mullard conductivity bridge, Type E.7566.

Figs 2 and 3 show the type of curves obtained for three sandstone cores from the same formation and for three representative limestone cores.

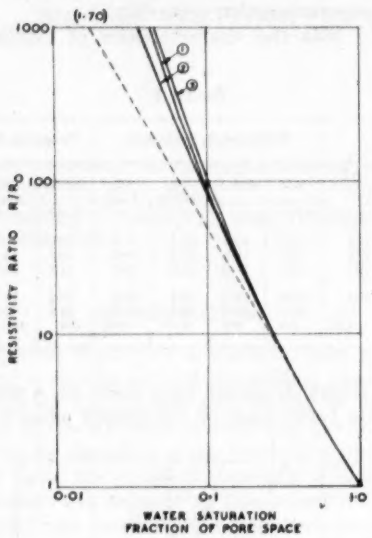

FIG 2

RESISTIVITY RATIO OF SANDSTONE CORES

Core	K, md	ϕ, %	F
1	208	20·4	13·1
2	274	17·0	18·0
3	268	15·2	21·6

In Fig 2 the resistivity curves show a departure from linearity (*i.e.*, where the simple power law $R/R_0 = S^{-1.7}$ holds) at water saturations of less than 30 per cent of the pore space. It is to be noted that most of the results reported in the literature are for a saturation range above 30 per cent, so that the curvature found here is not necessarily inconsistent with the normal acceptance of a straight line. Whether this upward curvature is due to the wettability characteristics of the rock or to the shape of the pore size distribution curve is not yet known. Imbibition tests did not show any marked tendency to preferential wettability to oil.

Studies on seven limestone cores of $k > 10$ md and $F < 20$ showed that the resistivity curves were reasonably linear, *i.e.*, where $R/R_0 = S^{-n}$, and the value of the slope n varied between 1·65 and 2·0. This range of values of n is very close to that reported by other workers, using sandstone cores.

Studies on twelve limestone cores of $k < 10$ md and $F > 20$, however, showed that there was pronounced curvature of the resistivity curves, and the departure from linearity is in the opposite direction to that for the sandstone cores in Fig 2. The reason for this curvature is different from that of the sandstones, and is probably due to the resistance of the rock being comparable with the fluid resistance at low saturation. The curvature is greatest where the formation factors to $CaSO_4$ and to NaCl are greatest.

If it is assumed that the true resistivity–saturation relationship is linear on a log–log plot, *i.e.*,

$$R_L/R_0{}^* = S^{-n}$$

where R_L is the fluid resistance at saturation S and $R_0{}^*$ is the fluid resistance at 100 per cent saturation of the pore space, then the apparent decrease in the slope n is due to the effect of the rock resistance R_S in parallel with the fluid resistance R_L.

The relation between $R_0{}^*$ and R_0 (where R_0 is the measured resistance of the fully saturated core) is

$$R_0{}^* = R_0/\{1 - (R_0/R_S)\} \quad . \quad . \quad (1)$$

The apparent resistance R at partial saturation S is

$$R = (R_L R_S)/(R_L + R_S) \quad . \quad . \quad (2)$$

and

$$R_L = R_0{}^* S^{-n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Eliminating $R_0{}^*$ the measured resistance ratio R/R_0 is given by

$$R/R_0 = 1/\{(R_0/R_S) + S^n[1 - (R_0/R_S)]\} \quad . \quad (4)$$

Fig 3 shows the effect of the rock resistance on the apparent resistivity–saturation curves for three limestone cores of widely different formation factors. The curves plotted to the above form of equation fit the experimentally measured points very well. The

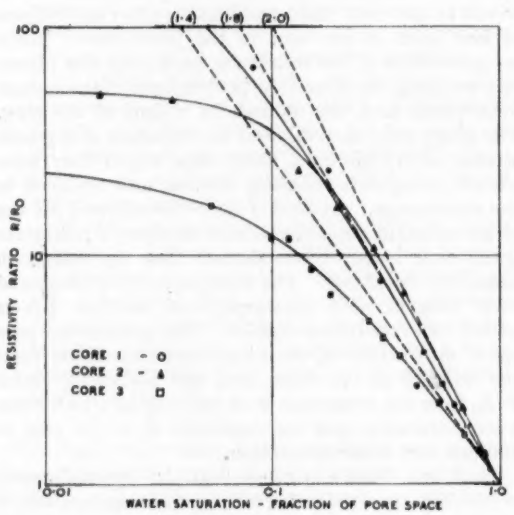

FIG 3

RESISTIVITY RATIO OF LIMESTONE CORES

Equation of curves :

$$R/R_0 = 1/[(R_0/R_S) + S^n(1 - R_0/R_S)]$$

Core	K, md	ϕ, %	F	R_S/R_0	n
1	902	26·3	13·2	200	1·8
2	1·0	14·7	50·8	52	2·0
3	0·09	4·0	159	23	1·4

specific resistance of the rock for the limestone samples was of the order of 10^4 ohm metres.

The method therefore allows the resistivity exponent n to be calculated from the initial slope of the resistivity–saturation curve, *i.e.*, at $S > 0{\cdot}5$ and the specific resistance of the rock from the curvature of the plot at $S < 0{\cdot}5$. It is realized that the resistance of the rock may change as the ionic content of the water changes, as will be apparent by changes in formation factor. These relationships and the effect of using saturated solutions of more soluble salts (to reduce the apparent curvature of the plots) are being investigated.

CONCLUSIONS

A satisfactory, rapid, and reproducible evaporation method has been developed for measuring the resistivity–water saturation characteristics of both sandstone and limestone core samples. Methods previously described in the literature were not suitable to the majority of limestone cores encountered, *i.e.*, of permeability less than 50 md. Results obtained have suggested the possibility of a more rigorous explanation for the deviation from linearity of the lower permeability limestone samples, and this is being investigated further.

ACKNOWLEDGMENT

The author wishes to thank the chairman and directors of Anglo-Iranian Oil Co. Ltd. for permission to publish this paper.

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[1] Archie, G. E. *Trans. Amer. Inst. Min. Engrs*, 1942, **146**, 54.
[2] Wyllie, M. R., and Spangler, M. B. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36**, 359. (This paper includes a comprehensive list of references.)
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THE INSTITUTE OF PETROLEUM

An Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 9 September 1953, the Chair being taken by the President, H. S. Gibson, C.B.E.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He then read the list of members elected since the previous meeting and various announcements.

The President, introducing the author of the paper to be presented, said: Mr. Porter, whom a great many of you may already know, or at any rate know of his work, graduated from the University of Wales in 1931. On leaving the University he became interested in shale oil and in particular its extraction from the Kimmeridge shales and then took up work in connexion with the development of processes for low temperature carbonization of coal. During the last war, he was employed on the production of explosives at Ranskill, and in 1944 joined the Anglo-Iranian Oil Company. His previous experience led him towards the development of catalytic hydrogenation processes, in particular the catalytic desulphurization of oils, and he is now to tell us about the development of the autofining process for which he has been largely responsible.

The following paper was then presented in summary by the author.

AUTOFINING: A NEW PROCESS FOR CATALYTIC DESULPHURIZATION

By F. W. B. PORTER *

SUMMARY

Autofining is a new process developed by the Anglo-Iranian Oil Company Ltd. for the catalytic desulphurization of petroleum distillates. The process embodies the feature that the hydrogen required for elimination of the sulphur as hydrogen sulphide is provided by dehydrogenation of certain compounds present in the feedstock. The process has been applied successfully to a variety of feedstocks up to the end of the gas oil boiling range (*ca* 360° C). The products need little or no after treatment, except for the removal of dissolved hydrogen sulphide.

The first commercial unit of 3500 b.d. capacity came on stream at the Llandarcy Refinery of National Oil Refineries Ltd. in July 1952. This paper gives details of the development work carried out at the AIOC Research Station, Sunbury, and a brief description of the commercial unit, with results of the operations to date.

INTRODUCTION

The removal, reduction, or conversion of sulphurous impurities from petroleum products has received the attention of the industry since the early days, and a number of processes are available which carry out the specific function which the refiner considers necessary. For example, in the refining of motor gasolines and kerosines it is necessary, in some cases, only to sweeten the product, and this can be conveniently performed by processes which convert the corrosive and odorous mercaptans into disulphides. If, on the other hand, elimination of sulphur is required with these products, *e.g.*, to improve the lead response or to prevent the formation of corrosive sulphur oxidation products on burning, it is necessary to have recourse to other treatments which remove the sulphur compounds, or to catalytic treatment which converts the sulphur to hydrogen sulphide.

Catalytic desulphurization without hydrogen or gas recycle, *e.g.*, the Perco [1] and Gray processes,[2] is known to desulphurize successfully the light distillates up to 200° C end-point. However, with the higher-boiling distillates, such as kerosine and gas oil, these processes are less successful, and only short on-stream times are possible. The high temperatures which have to be employed with the heavier distillates tend to produce unstable products.

For some time the AIOC has been engaged in research in the development of a process for catalytic desulphurization, with particular emphasis on gas oils or diesel engine fuels. It was well known that high-pressure hydrogenation converted sulphur to hydrogen sulphide, but the reaction was accompanied by a considerable breakdown in molecular structure, and this was most undesirable from the view of product quality. However, a very satisfactory process at lower pressures was developed, and it was found possible, by suitable changes in operating conditions, to desulphurize all straight-run distillates more or less completely without any adverse change in product quality. A considerable degree of desulphurization was also obtained with crude oil residue feedstocks. The pressures employed were relatively low, 500 to 1000 p.s.i.g., and the equipment was therefore obtainable at a reasonable cost. The only disadvantage of this process was its consumption of hydrogen, the amount required being proportional to the sulphur removed and the nature of the sulphur compounds. The future development of the hydrofining process would appear to depend upon the provision of cheap hydrogen, which is not yet generally available.

From the work on the hydrofining process, it was known that the amount of hydrogen required for desulphurization was small, being of the order of 70 cu. ft/brl for the removal of 1·0 per cent weight sulphur in the feedstock. As all the crude oils

* Anglo-Iranian Oil Co. Ltd.

contain naphthene hydrocarbons in varying degree throughout the boiling range, it was considered that if the dehydrogenation of these naphthenes could be carried out under mild conditions to ensure long on-stream hours, then hydrofining should be possible at the same time, and the desulphurization reaction could become self-supporting with respect to hydrogen. From the meagre thermodynamic data available, it was known that dehydrogenation of six-membered ring naphthenes was theoretically complete above 350° C (660° F) and that the recycle of hydrogen, *per se*, had little effect on the reaction, but increase in the partial pressure of hydrogen retarded the reaction, having a marked effect above 250 p.s.i. During the work on the hydrofining process, highly active desulphurizing catalysts had been developed, and it was considered that with these a high sulphur removal would be possible, even at the low partial pressures of hydrogen which were contemplated as essential to ensure adequate dehydrogenation.

It was realized that the major interest of the process, from a commercial point of view, would lie in the desulphurization of the higher-boiling distillates and those materials requiring relatively extensive refining treatment, although early work was carried out on light feedstock. A detailed study of the hydrocarbon type analyses of naphthas and kerosines gave indications of the presence of easily dehydrogenatable naphthenes, and the possible operating conditions could be forecast with some confidence. In the case of the heavier feedstocks, such as gas oils, little was known, and only a rough guess could be made of the possible operating conditions.

The main objective of the development work was a catalytic desulphurization process which would retain the advantages of the hydrofining process and, at the same time, be self-supporting with respect to hydrogen. The essentials of the process were considered to be :

(1) It should be self-supporting with respect to hydrogen.

(2) The conditions of operation should be such that little or no molecular breakdown occurred, and the product, except for sulphur elimination, should have properties and boiling range similar to the feedstock.

(3) On-stream time should be sufficiently long to avoid frequent regeneration; a minimum of 200 hours was aimed at.

(4) The process should be capable of handling a wide range of feedstocks so as to provide flexibility in refinery operations.

The process was termed "autofining," a shortened and convenient version of the more logical term "auto-hydrofining."

The laboratory work at the Research Station of the AIOC resulted in the development of a very satisfactory desulphurization process capable of handling most distillate feedstocks. Before the final design of a large-scale unit was formulated, investigations on the 150-b.d. pilot-plant scale were also carried out, principally to provide additional chemical engineering data and to confirm estimates of catalyst life. The pilot plant investigations were carried out at the Grangemouth Refinery of Scottish Oils Ltd., and on the completion of these tests the unit was enlarged to 350-b.d. capacity, and used for the desulphurization of an aromatic extract on a commercial scale. Subsequently, the first large-scale unit of 3500-b.d. capacity, designed to handle naphthas and power kerosines, came on stream in July 1952 at the Llandarcy Refinery of National Oil Refineries Ltd.

The process has been fully covered by patents in all major countries.

DESCRIPTION OF THE PROCESS

The autofining process, as finally developed, can be best defined as a process for the catalytic desulphurization of petroleum distillates operating at moderate pressures and temperatures, in which the sulphur compounds are preferentially attacked and converted into non-substituted molecules by the action of hydrogen, and in which the hydrogen required is provided by dehydrogenation of part of the feedstock itself. The non-hydrocarbon, *e.g.*, sulphur, is removed in the form of hydrogen sulphide, which can easily be separated from the other reactants.

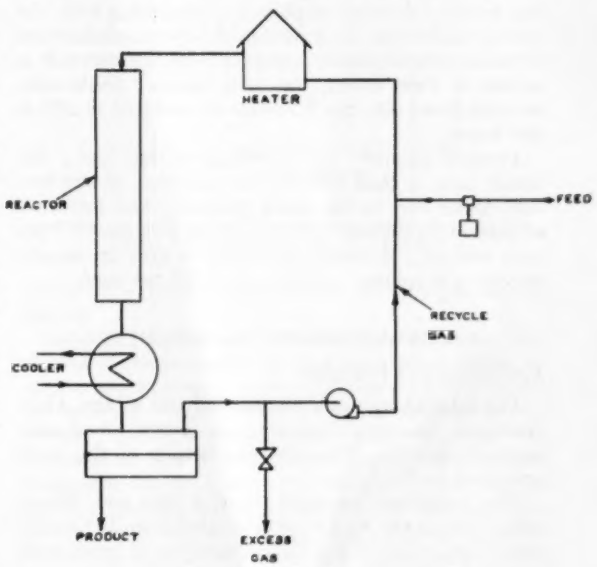

FIG 1

THE AUTOFINING PROCESS—FLOW DIAGRAM

The gases, which consist mainly of hydrogen and are continuously recycled, join the cold feed before the heater (Fig 1). After vaporization and superheating to the required operating temperature, the vapours pass downwards through the catalyst bed, where the reactions take place. After cooling, the separated gases are recycled to the process, and the

liquid product is stabilized for the removal of dissolved gases and hydrogen sulphide. Pressure control of the process is maintained by venting off the excess gas before recycling. It is not essential to remove hydrogen sulphide from the recycle gases, and it is preferable to allow this gas to reach equilibrium, so that all sulphur removed from the feedstock is obtained as hydrogen sulphide dissolved in the liquid product at plant pressure.

The two reactions, dehydrogenation and desulphurization, are endo- and exo-thermic respectively, so that the overall reaction is substantially thermoneutral.

The preferred type of catalyst is that of mixed cobalt and molybdenum oxides on alumina. Catalysts of this type can be regenerated *in situ* with steam–air or inert gas–air mixtures when the original activity of the catalyst is fully restored. Processing periods depend upon the boiling range of the feedstock and the space velocities employed; generally, with the lighter feedstocks, such as straight-run naphthas and kerosines, regeneration is required only at intervals in excess of 1000 hours, but with heavier feedstocks, such as diesel oils, the intervals are reduced to 200 to 400 hours.

Product recovery on autofining is very high; the major loss is that due to the removal of sulphur. Any losses due to the small gas-make and lay-down of carbon on the catalyst are usually less than 0·1 per cent weight. A small reduction in gravity usually results in a volume recovery of *ca* 100 per cent.

LABORATORY-SCALE STUDIES

Equipment and Procedure

The laboratory work was carried out at the AIOC Research Station, Sunbury, on three small-scale catalytic plants. The essential details of the units are given in Fig 2.

The isothermal reactors are of 1 litre and 500 ml catalyst capacity, and were fabricated from 18 Cr–8 Ni steel tube. One of the main difficulties in small-scale operations of this nature is the recycle of gases at constant rate without disproportionate losses. The general level of excess gas-make is low at the small throughputs employed in laboratory work, and even a small loss cannot be tolerated. A small booster was therefore designed, utilizing the principle of the displacement-type plunger pump with a liquid seal on the glands.[3]

The procedure adopted was to charge the reactor with the requisite amount of 4- to 8-mesh catalyst, and after pressure testing, the unit was pressured up with hydrogen to the desired operating level, and gas recycle commenced. The introduction of hydrogen at this stage was purely a matter of convenience to enable the study of process variables to be carried out under identical conditions. The process can be started by recycling refinery or other gases before injecting the feed, and this procedure was adopted on the pilot plant and on the large-scale unit. The reactor and preheater were then brought to operating temperature, and the feed started. The hot vapours from the reactor were separated at operating pressure after passing through the water cooler. The cooled gases were fed back to the booster and the liquid product let down to atmospheric pressure, when most of the dissolved gases were removed. The liquid product was then either washed with caustic soda and water or stabilized to remove the remaining hydrogen sulphide. Excess gas-make was removed from the system via a control valve, which maintained the unit at the desired operating pressure.

Process Variables

The two reactions involved in the process are dehydrogenation and desulphurization: the dehydrogenation reaction is increased by raising the temperature and suppressed by increase of pressure; desulphurization is increased by additional hydrogen partial pressure, and has an apparent maximum in

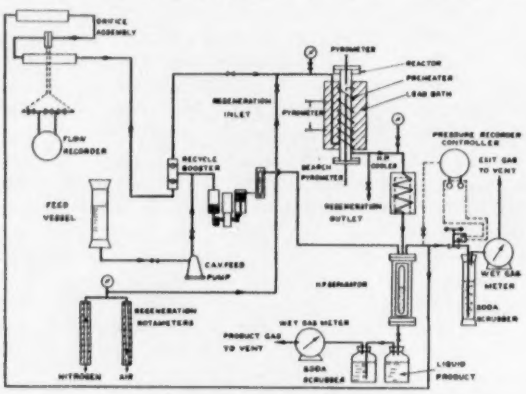

FIG 2
SMALL-SCALE CATALYTIC PLANT

the temperature range 760° to 780° F for all feedstocks. Extensive dehydrogenation leads to a marked change in product quality, and therefore high temperatures are to be avoided. The employment of high pressures at moderate temperatures, while leading to a corresponding increase in desulphurization, may result in suppression of the dehydrogenation activity to a point where the reaction is not self-supporting with respect to hydrogen; under these conditions, the plant pressure would drop until equilibrium was reached between the two simultaneous reactions.

In general, with increase in boiling range and sulphur content of the feedstock, the temperature and pressure limitations of the process became correspondingly closer. This can be to some extent modified by the employment of cuts of wide boiling range where the lower-boiling fractions provide the necessary hydrogen to desulphurize the heavier fractions.

In the case of the lower-boiling, straight-run distillates, *e.g.*, naphthas and kerosines, desulphuriza-

tion is virtually complete at low pressure (100 p.s.i.g.), temperatures between 750° to 800° F, and space velocities of 5·0 vol/vol/hr. It is obvious, therefore, that the effect of changes in process variables will be relatively small, and the choice of conditions is primarily governed by economic considerations and the throughput required. In common with all catalytic desulphurization processes, the products are marginally doctor-positive, but sweeten on storage. The processing hours with feedstocks of this type are upwards of 1000 without loss in desulphurizing activity.

With the higher-boiling and consequently high sulphur feedstocks, the effects of the process variables are considerable. The temperature and pressure variables have a marked effect on the desulphurization and dehydrogenation reactions, as can be seen from Figs 3 to 6.

The temperature variable was examined with a gas oil–kerosine blend, whereas the pressure variable refers to a gas oil feedstock; the latter, being a more refractory and higher sulphur feedstock, shows up the pressure effect more clearly. The residual sulphur content is approximately inversely proportional to the plant pressure, or, more correctly, to the hydrogen partial pressure, a result analogous to that obtained during hydrofining operations at higher pressures.

Space velocity, *i.e.*, volumes of oil/volume of catalyst/hour, has little effect on low sulphur content feedstocks for the reason mentioned previously, but, in the case of the higher-boiling and higher sulphur

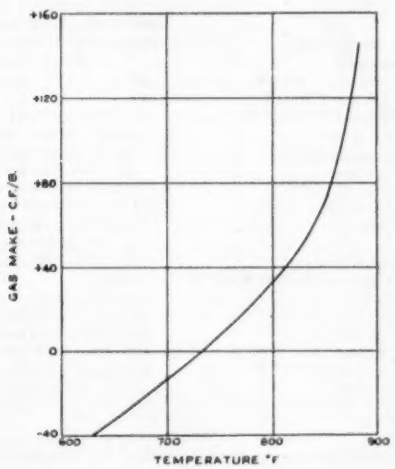

FIG 3

EFFECT OF TEMPERATURE ON GAS-MAKE AUTOFINING OF KEROSINE–GAS OIL FEEDSTOCK

feedstocks, the residual sulphur has been found to be approximately directly proportional to the space velocity in the range 1 to 4 vol/vol/hr.

The effect of change of recycle rate is not marked, although there is a definite trend towards lower gas-make and higher desulphurization with increase in recycle rate. This is probably due to the slightly increased hydrogen partial pressure. High recycle rates increase the on-stream hours before regeneration, but there are obvious mechanical advantages in keeping the rate as low as possible, and these would

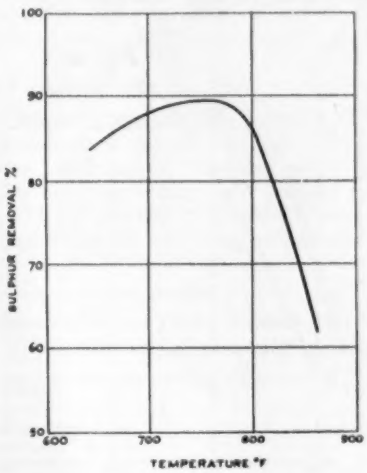

FIG 4

EFFECT OF TEMPERATURE ON DESULPHURIZATION AUTOFINING OF KEROSINE–GAS OIL FEEDSTOCK

probably outweigh any process advantage that is gained.

Another important consideration effecting the success of the process is the number of permissible on-stream hours before it becomes necessary to regenerate the catalyst. Again, with the lighter feedstocks, the process variables have little effect, provided the temperature and pressure conditions are kept within reasonable limits, *e.g.*, 50 to 200 p.s.i.g. and 750° to 800° F. Temperatures above 800° F increase the carbon lay-down and cause rapid loss of activity. Processing-periods of 800 hours have been carried out with no loss of activity on these feedstocks.

With the higher-boiling and higher sulphur-content feedstocks, such as aromatic extracts, gas oils, and blends containing these materials, a slow but significant decline in catalyst activity with hours on stream is experienced. Up to the present, it has not been found possible to overcome this difficulty, but the proper choice of process conditions has enabled on-stream times of upwards of 200 hours to be attained; the hours on stream are also dependent upon the level of desulphurization required. Regeneration completely restores the catalyst activity.

From the work on the process variables, it was possible to lay down a set of process conditions under which the majority of feedstocks could be economically desulphurized. These were:

Pressure	50 to 200 p.s.i.g.
Temperature . . .	750° to 800° F
Space velocity . . .	1·0 to 5·0 vol/vol/hr
Recycle rate . . .	2000 to 4000 cu. ft/brl

All of this work was carried out on catalysts of the type composed of mixed cobalt and molybdenum oxide on alumina with a $MoO_3 : CoO$ ratio of 5 : 1; experiments with a large number of other catalysts showed that this type was the most efficient. A large number of experiments has shown that regeneration of these catalysts with steam–air or inert gas–air mixtures restored the original activity of the catalysts, up to 30 regenerations having no significant effect on activity.

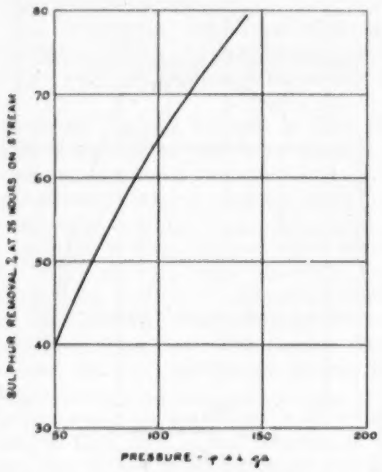

FIG 5

EFFECT OF PRESSURE ON DESULPHURIZATION AUTOFINING OF GAS OIL

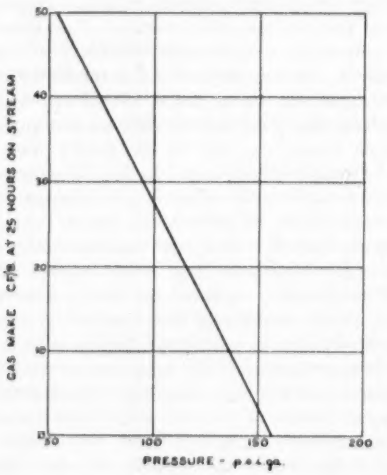

FIG 6

EFFECT OF PRESSURE ON GAS-MAKE AUTOFINING OF GAS OIL

Theoretical calculations showed that, under conditions which result in no excess gas and when 1 per cent weight of sulphur is removed from the feedstock, the heat of reaction is slightly endothermic, to the extent of *ca* 650 B.Th.U/brl feedstock processed; this would result in a drop of temperature of 3° F in the reactants. A further endothermic heat of reaction equivalent to *ca* 700 B.Th.U/brl is to be expected from each 10 cu. ft/brl of excess gas-make. If a slight amount of cracking takes place and this is followed by hydrogenation, an overall exothermic reaction ensues, so that, on balance, the autofining process is practically thermoneutral under ideal adiabatic conditions.

FEEDSTOCK SURVEY

The process has been applied to a large variety of feedstocks from Middle East crudes; the following paragraphs give details of the results obtained.

Straight-run Naphthas

All the naphtha feedstocks, *i.e.*, up to *ca* 200° C ASTM end-point, can be more or less completely desulphurized at 5·0 vol/vol/hr, 100 p.s.i.g. and 780° F (Table I).

TABLE I

Autofining of Iranian Straight-run Gasoline

Conditions :		
Processing period, hr		800
Temperature, ° F		780
Pressure, p.s.i.g.		100
Space velocity, vol/vol/hr		5·0
Recycle rate, cu. ft/brl		2000
Gas make (average)		10
Gas mol % H_2		90
	Feedstock	Product
Yield, % wt on feed	100·0	99·5
Inspection data :		
Octane number, ASTM	60	62·3
plus 1·5 ml T.E.L/I.G.	69	75
plus 3·5 ml T.E.L/I.G.	75	81
Sulphur, % wt	0·081	0·0007
Sulphur removal, %	—	99·1
Colour Saybolt	—	>+30
Aromatics, % wt	7·7	7·8
Bromine number	<1	2
Doctor test	—	Negative
Odour	—	Merchantable
Corrosion (Cu strip)	—	No change
Specific gravity at 60° F/60° F	0·696	0·700
Distillation :		
I.B.P., ° C	27	26
5% vol at ° C	40	39
10% vol at ° C	47	46
50% vol at ° C	93	93
90% vol at ° C	132	132
F.B.P., ° C	149	150

Desulphurization is accompanied by an increase in clear octane number and greatly improved lead response. No loss of desulphurization activity has been observed for processing periods of 800 hours without regeneration. An important application of the process, apart from the obvious one of motor gasoline components, is to the production of special boiling products and white spirits. The products after distillation to the desired boiling range are of excellent quality (Table II).

TABLE II

Autofining of Iranian Straight-run Naphtha for White Spirit Production

Conditions:	
Processing period, hr	400
Temperature, ° F	780
Pressure, p.s.i.g.	100
Space velocity, vol/vol/hr	5·0
Recycle rate, cu. ft/brl	2000
Gas make (average)	22
Gas mol % H_2	95

	Feed-stock	Autofined product	White spirit cut
Yield, % wt on feed	100	99·7	72·1
Inspection data:			
Total sulphur, % wt	0·116	0·0019	0·0005
Sulphur removal, %	—	98·4	—
Colour Saybolt	—	+26	+30
Aromatics, % wt	17·8	19·3	18·3
Bromine number	1	1	2
Doctor test	—	Negative	Negative
Odour	—	Merchant-able	Merchant-able
Corrosion (BSI)	—	—	Passes
Corrosion (Reactive S)	—	—	No change
Specific gravity at 60° F/60° F	0·780	0·779	0·782
Distillation:			
I.B.P., ° C	148	140	158
5% vol at ° C	154	151	160
10% vol at ° C	156	153	161
50% vol at ° C	167	165	167
90% vol at ° C	187	187	179
F.B.P., ° C	206	209	193

TABLE III

Autofining of Iranian Kerosine

Conditions:	
Processing period, hr	400
Temperature, ° F	780
Pressure, p.s.i.g.	100
Space velocity, vol/vol/hr	5·0
Recycle rate, cu. ft/brl	2000
Gas make (average), cu. ft/brl	18
Gas mol % H_2	91

	Feedstock	Product
Yield, % wt on feed	100·0	99·5
Inspection data:		
Total sulphur, % wt	0·180	0·004
Sulphur removal, %	—	98·0
Mercaptan sulphur, % wt	0·016	<0·001
Colour Saybolt	+15	+17
Flash point, ° F	126	106
Aromatics, % wt	16·9	17·8
Bromine number	2	2
Odour	Unmerchant-able	Merchant-able
Doctor test	Positive	Negative
Smoke point, mm	25	26
Burning test:		
Consumption, g/hr	20·6	20·1
Char, mg/kg	28	14
Glass	Grey-brown film	Very faint grey film
Specific gravity at 60° F/60° F	0·799	0·798
Distillation:		
I.B.P., ° C	169	165
2% vol at ° C	178	174
10% vol at ° C	185	184
50% vol at ° C	207	206
90% vol at ° C	230	231
F.B.P., ° C	244	247

Kerosines

These feedstocks, boiling range *ca* 160° to 260° C, are also easily desulphurized under conditions similar to those employed for naphtha feedstocks; in addition to the elimination of sulphur the char value is considerably reduced (Table III).

On sulphur-dioxide extraction of the autofined kerosine for the removal of aromatics, a first-grade burning oil is obtained, together with an aromatic extract of low sulphur content, which is a valuable component for motor gasoline or tractor vaporizing oil blends.

Tractor Vaporizing Oils

These materials are naphtha–kerosine blends, containing a suitable proportion of a high octane number-component, such as an aromatic extract or high-boiling fraction from catalytically cracked naphthas.

Table IV contains the details of a typical run on a tractor vaporizing oil containing an aromatic extract.

TABLE IV

Autofining of Iranian Tractor Vaporizing Oil Blends

Sample	Containing 45% vol of SO_2 extract		Containing 25% vol cat-cracked naphtha	
Conditions:				
Processing period, hr	400		50	
Temperature, ° F	780		800	
Pressure, p.s.i.g.	100		100	
Space velocity, vol/vol/hr	3·0		0·5	
Recycle rate, cu. ft/brl	2000		7000	
Gas make (average) cu. ft/brl	2·4		47·8	
Gas mol % H_2	78·2		58·5	
	Feed-stock	Product	Feed-stock	Product
Yield, % wt on feed *	100·0	97·0	100·0	96·0
Inspection data:				
Sulphur, % wt	0·577	0·126	1·43	0·09
Sulphur removal, %	—	78·2	—	93·6
Octane number (M.M.)	48·1	51·2	47·2	56·0
Colour Saybolt	−6	+20	−10	+18
Corrosion (Cu strip)	Passes	Passes	—	Passes
Gum preformed, mg/100 ml	—	5	—	17
Gum potential, mg/100 ml	—	Trace	—	6
Specific gravity at 60° F/60° F	0·824	0·821	0·836	0·829
Distillation:				
I.B.P., ° C	151	149	166	146
5% vol at ° C	—	—	181	161
10% vol at ° C	165	164	185	169
50% vol at ° C	185	186	218	208
90% vol at ° C	243	244	255	256
F.B.P., ° C	292	284	270	284

* Approximately 2% vol bottoms removed in knock-out drum.

Processing conditions are similar to those employed for kerosine and naphthas except for a slightly lower space velocity on account of the higher sulphur content. A gradual decline in catalyst activity with hours on stream is experienced with these feedstocks (Fig 7), but even so an average sulphur removal of 78 per cent (from 0·6 to 0·13 per cent weight) can be obtained over 400 hours.

As the Pool specification for sulphur content is

0·35 per cent weight, it is clear that even longer on-stream hours can be tolerated. In addition to the sulphur removal, a gain of 2 to 3 octane numbers is obtained.

Tractor vaporizing oil blends containing a catalytically cracked naphtha component are more difficult to autofine. Owing to the high sulphur content of this component, a much reduced space velocity and a higher temperature have to be employed. However, the large octane number increase obtained makes it possible to reduce the proportion of the catalytic cracker component, giving a relatively larger amount of the hydrogen-donating fractions. A typical result with a blend containing 25 per cent volume of catalytically cracked naphtha of 4·5 per cent weight sulphur content is given in Table IV.

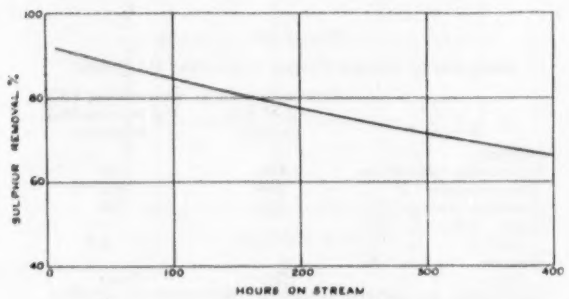

FIG 7

EFFECT OF HOURS ON STREAM ON DESULPHURIZATION TRACTOR VAPORIZING OIL FEEDSTOCK

The sulphur removal obtained (93·6 per cent) was excellent, and this was accompanied by an increase of 8 to 9 octane numbers (clear). Thus, a valuable outlet has been found for a fraction which it is virtually impossible to refine by normal methods and would otherwise be degraded to a fuel oil component.

Aromatic Extracts

These materials are prepared by the treatment of naphtha and kerosine fractions with liquid sulphur dioxide. They are highly aromatic (>75 per cent weight), and are valuable components of aviation and motor spirit blends and tractor vaporizing oils. The heavier extracts have relatively high sulphur contents, and a fairly extensive treatment is normally required to meet specification.

The lighter extracts, *e.g.*, benzine extract, react to the process in a similar manner to the light, straight-run distillates. Virtually complete desulphurization (from 0·3 to 0·004 per cent weight sulphur content) being obtained at 3·0 vol/vol/hr, 780° F, and 100 p.s.i.g. (Table V). A clear octane number increase of 2 is obtained, and the autofined product can be used in aviation gasolines without further treatment.

With the heavier extracts, desulphurization depends to some extent on the boiling range and sulphur content. An extract of 155° to 260° C ASTM boiling range, when autofined at 780° F, 100 p.s.i.g., and 2·0 vol/vol/hr, gave an average sulphur removal of 92 per cent over 200 hours on stream (from 0·7 to 0·05 per cent weight sulphur).

TABLE V

Autofining of Iranian SO_2 Extracts

Sample	Benzine extract		Kerosine extract	
Conditions :				
Processing period, hr	200		200	
Temperature, ° F	780		780	
Pressure, p.s.i.g.	100		100	
Space velocity, vol/vol/hr	3·0		2·0	
Recycle rate, cu. ft/brl	2000		2000	
Gas make (average), cu. ft/brl	4·2		6·0	
Gas mol % H_2	85		76·5	
	Feed-stock	Product	Feed-stock	Product
Yield, % wt on feed *	100·0	97·5	100·0	97·0
Inspection data :				
Sulphur, % wt	0·295	0·004	0·692	0·052
Sulphur removal, %	—	98·6	—	92·5
Octane number (M.M.)	85·3	87·2	—	—
Colour Saybolt	+15	+27	0	+22
Aromatics,† % wt	78·1	76·2	75·5	73·8
Bromine number	2	1	—	—
Gum existent, mg/100 ml				
Gum E + P, mg/100 ml	1	1	—	—
Specific gravity at 60° F/60° F	0·836	0·835	0·869	0·864
Distillation :				
I.B.P., ° C	115	110	155	141
5% vol at ° C	119	117	165	159
10% vol at ° C	120	119	170	164
50% vol at ° C	129	127	189	187
90% vol at ° C	145	144	233	233
F.B.P., ° C	163	164	254	258

* Approximately 2% vol bottoms removed in knock-out drum.

† Includes sulphur compounds.

A heavier extract of 160° to 290° C ASTM boiling range with a sulphur content of 1·0 per cent weight, when autofined at 3·0 vol/vol/hr, gave an average desulphurization over 200 hours of 64 per cent; the sulphur removal falling from 75 to 52 per cent over the period. With this type of feedstock, it was not found possible to operate at a pressure above 70 to 80 p.s.i.g., this being the equilibrium pressure at which the hydrogen make balanced the sulphur removal. This type of operation, termed equilibrium pressure operation, has advantages in that it makes full use of any hydrogen make. It is discussed further in the next subsection.

The autofined aromatic products also show a gain in clear octane number of 2 to 3 numbers (Table V).

Gas Oils

The gas oils examined are primarily used as high-speed diesel fuels; they are straight-run distillates of *ca* 200° to 350° C ASTM boiling range, and their sulphur content ranges from 0·7 to 1·0 per cent

weight for fractions from Middle East crudes. This type of fuel is in increasing demand for diesel-engined road vehicles, and the supply is limited by the necessity to keep the end-point low, in order that the sulphur content may not exceed the marketing specifications. It is clear, therefore, that an increased volume of gas oil could be marketed if desulphurization could be accomplished. The development of the hydrofining process by the AIOC was largely concerned with gas oil feedstocks, and so with the autofining process a considerable effort was made to examine closely the effect of the process variables with this feedstock.

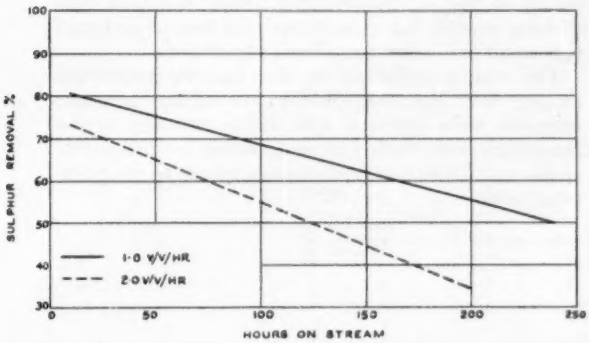

FIG 8

EFFECT OF SPACE VELOCITY AT 4000 CU. FT/BRL GAS RECYCLE ON AUTOFINING GAS OIL FEEDSTOCKS (1·0% WT SULPHUR)

The effect of pressure was discussed in an earlier section (Figs 5 and 6), while the temperature effects were similar to those shown for a kerosine–gas oil blend (Figs 3 and 4). With gas oil feedstocks temperatures above 800° F cause considerable cracking and breakdown; 780° F is considered to be the optimum temperature at 100 p.s.i.g. pressure to give reasonably long on-stream time.

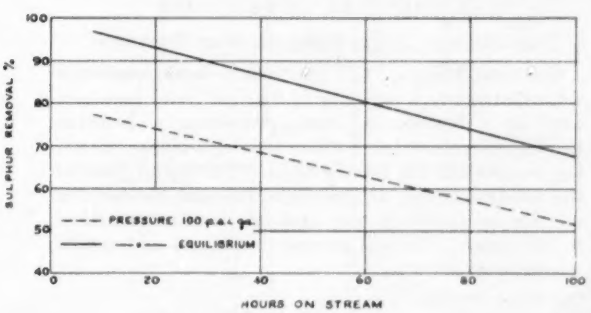

FIG 9

EFFECT OF EQUILIBRIUM PRESSURE OPERATION ON DESULPHURIZATION AUTOFINING OF GAS OIL FEEDSTOCK AT 780° F AND 2·0 VOL/VOL/HR

The effect of space velocity is shown in Fig 8.

The proper choice of operating conditions depends upon the level of desulphurization required; if a moderate level (50 per cent) is required, then a space velocity of 2·0 can be employed over processing periods of 200 hours.

Typical data on bulked samples of autofined gas oils are given in Table VI.

TABLE VI

Autofining of Iranian Gas Oils

Sample	A		B	
Conditions:				
Processing period, hr	200		200	
Temperature, ° F	780		780	
Pressure, p.s.i.g.	100		100	
Space velocity, vol/vol/hr	2·0		2·0	
Recycle rate, cu. ft/brl	2000		2000	
Gas make (average), cu. ft/brl	15·1		5·0	
Gas mol % H_2	80		79·5	
	Feed-stock	Product	Feed-stock	Product
Yield, % wt on feed	100·0	99·4	100·0	99·2
Inspection data:				
Sulphur, % wt	0·720	0·360	1·0	0·48
Sulphur removal, %	—	50·0	—	52·0
Mercaptan sulphur, % wt	0·011	0·001	0·07	0·002
Diesel index	60	60	55	56
Cetane number	54	54	54	54
Flash point, ° F	186	168	225	205
Pour point (upper), ° F	15	10	15	15
Conradson carbon (10% res.), % wt	0·08	0·13	0·11	0·12
Aniline point, ° F	161	159	160	160
Copper strip at 100° C	Passes	Passes	Passes	Passes
Specific gravity at 60° F/60° F	0·839	0·836	0·854	0·850
Distillation:				
I.B.P., ° C	208	185	237	198
5% vol at ° C	—	—	266	250
10% vol at ° C	230	226	271	262
50% vol at ° C	270	265	294	291
90% vol at ° C	330	325	326	323
F.B.P., ° C	357	357	350	350

Stabilization to remove dissolved gases and hydrogen sulphide is the only treatment necessary to produce specification products.

The normal method of operation with gas oil feedstocks is to pressure the unit with recycle gas from a previous operation, or by starting from atmospheric pressure with a naphtha feedstock until sufficient recycle gas has been made to bring the pressure to 100 p.s.i.g., when the change-over to gas oil can be made; both methods have been carried out with equal success. Thereafter, any excess gas (which is *ca* 80 per cent hydrogen) is removed from the system to maintain the pressure at 100 p.s.i.g. Normally, even with gas oil feedstocks, sufficient excess gas is made during the first 20 hours which, when stored, is adequate for purging and starting up. Consequently, a considerable quantity of hydrogen is vented which could be usefully employed in removing more sulphur. To avoid the wastage of this hydrogen and to ensure that maximum desulphurization is obtained, operation under equilibrium-pressure conditions can be employed. Under these conditions, no gas is removed

from the system, and the pressure is allowed to reach equilibrium. The effect on desulphurization is marked, as can be seen from Fig 9. The operation was carried out with a gas oil feedstock of 0·9 per cent weight sulphur content at 780° F, 2 vol/vol/hr, and 2000 cu. ft/brl recycle gas. Fig 10 shows that a maximum pressure of 200 p.s.i.g. was reached in this particular experiment.

PILOT PLANT INVESTIGATIONS

Investigation of the autofining process was limited at Sunbury, where only laboratory-scale operations could be carried out, and before a detailed design for a big unit could be made, work on a larger scale was necessary. A 150-b.d. unit was erected, therefore, at the Grangemouth Refinery of Scottish Oils Ltd.

The reactors in use on the laboratory units at Sunbury were of isothermal design. In large-scale plants, this method of operation is impracticable, and it was therefore of great importance to determine the true extent of the heat of reaction when operating under adiabatic conditions; a theoretical estimation of the thermal effect has been given in an earlier section. In addition to the study of the heat of reaction and other chemical engineering problems, it was necessary to study process-operating technique and variables, in particular the catalyst life and its resistance to breakdown and repeated regeneration.

Before the unit could be operated, the necessary catalyst charge (7 cu. ft.) had to be obtained. It was thought inadvisable at this stage, when only relatively small quantities of catalyst were involved, to rely solely on an outside chemical manufacturer, and it was decided therefore to manufacture the first charge of catalyst at Sunbury. This added considerably to our knowledge of the preparation of catalysts of this type (impregnated mixed cobalt and molybdenum oxide on alumina), and this information was passed on when the manufacture of large batches of catalyst was contemplated.

The pilot plant was designed for a throughput of 150 b.d. at 5·0 vol/vol/hr, with a maximum working pressure of 200 p.s.i.g. A simplified flow diagram of the unit is given in Fig 11.

The unit was operated successfully for over twelve months, during which time a variety of feedstocks was processed. A total on-stream time of 5500 hours and thirty-three regenerations were completed, and a sample of catalyst, withdrawn from the reactor and tested in the laboratory unit under standard conditions, showed less than 5 per cent loss of activity; this small loss is not considered significant.

The results obtained on the various feedstocks, ranging from light naphthas to gas oil and aromatic extracts, were identical with those obtained in the laboratory-scale work, and no apparent loss of activity ensues on translation from the laboratory to the pilot-plant scale.

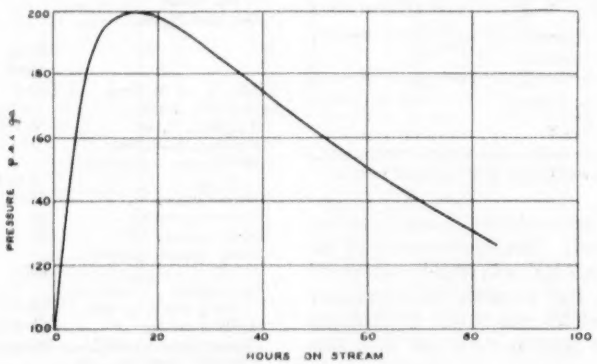

FIG 10

PLANT PRESSURE–EQUILIBRIUM PRESSURE OPERATION AUTOFINING OF GAS OIL FEEDSTOCK

COMMERCIAL OPERATIONS

THE 350-B.D. UNIT, GRANGEMOUTH REFINERY

On completion of the pilot-plant work, this unit was enlarged to a capacity of 350 b.d., and has been used as a commercial unit, processing a kerosine sulphur dioxide extract which is a high-octane blending component for tractor fuels. The major part of the catalyst charge at present in the unit has been in use for *ca* 16,000 hours, and has been regenerated *ca* 100 times. Typical process conditions and results on this unit are:

Operating Conditions:	
Space velocity	3·0 vol/vol/hr
Temperature	780° F
Pressure	*ca* 100 p.s.i.g.
Gas recycle rate	2000 cu. ft/brl
Processing period	200 hr
Regeneration	Steam–air mixtures

Inspection Data:	Feedstock	Product
Specific gravity at 60° F/60° F	0·870	0·867
I.B.P., °C	164	154
10% vol at °C	175	175
50% vol at °C	197	195
90% vol at °C	252	251
F.B.P. at °C	295	297
Total sulphur, % wt	1·04	0·45
Sulphur removal, %	—	56·8
Octane number (M.M.) clear	76	77

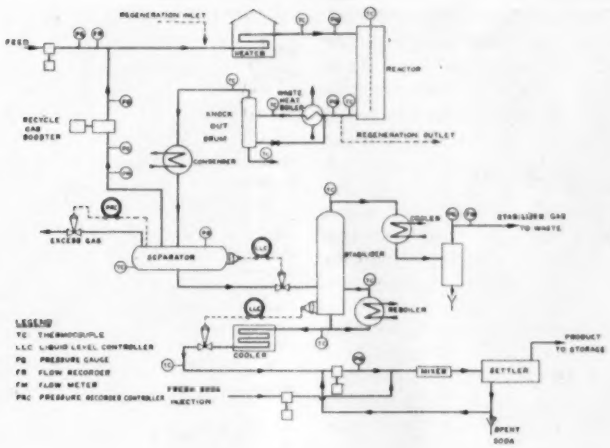

FIG 11

150-B.D. AUTOFINING PILOT PLANT

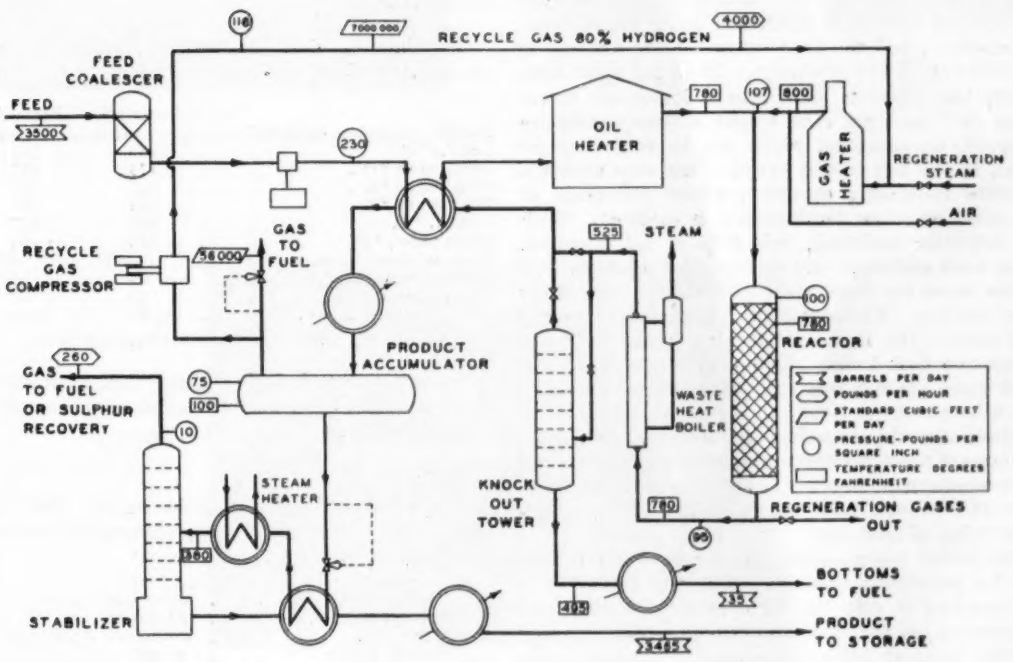

FIG 12

FLOW SHEET OF 3500-B.D. AUTOFINING UNIT

The 3500-b.d. Unit, Llandarcy Refinery

This unit was commissioned in July 1952 at the Llandarcy Refinery of National Oil Refineries Ltd. and was designed to operate on naphtha and tractor fuel in blocked operation. The autofined naphtha is an intermediate product, which is subsequently distilled in conventional refinery equipment for special products, but the power kerosine is obtained from the unit as a finished product ready for the market. A simplified flow sheet of the unit is given in Fig 12 and Figs 13 to 15 give views of the more important items of the equipment. In this unit, the feedstock and recycle gases are raised to the reactor temperature in separate heaters. This is done for two reasons:

(1) To reduce the pressure drop to be handled by the recycle compressors.

(2) To restrict the employment of stainless steel which is necessary to combat the corrosion caused by the hydrogen sulphide in the recycle gases.

The superheated vapours then pass downwards through a bed of 7·4 tons of catalyst of the mixed cobalt and molybdenum oxides on alumina type. The reactor vessel is of mild steel, and has a 4-inch internal refractory lining. The hot vapours from the reactor pass through a waste-heat boiler where steam is generated, and the temperature of the vapours is reduced to near the dew point. From the waste-heat boiler, the products pass into a knock-out tower where *ca* 1 to 2 per cent weight of heavy ends are removed, an operation which can be controlled by reflux to the top of the tower. This step avoids a separate re-running operation where correction of end-point or colour improvement is required. With the naphtha feedstock, this step is not required. After heat exchange and cooling, the products flow to the separator from which the recycle compressor takes suction. Excess gas-make is passed to the gas fuel main. The liquid product from the separator passes to a flash tower, where hydrogen sulphide and other gases are removed and flash point rectification can take place. A light caustic soda wash is given to guard against poor stabilizer operation. Generally, all items of the equipment in contact with recycle gas at temperatures above *ca* 500° F are constructed from 18 : 8 Cr–Ni steel, the remainder of the equipment being of mild steel.

The initial commissioning of the unit was carried out by processing naphtha. External hydrogen is not required to start up the unit, since refinery gas is recycled via the compressors and furnace to heat up the catalyst before commencing naphtha feed. Thereafter, the volume of gas retained in the separator, which is purposely designed oversize, is sufficient for bringing the unit on stream after regeneration. The actual commissioning of the unit was carried out smoothly and without incident.

The design conditions for the unit on both feedstocks are:

Pressure	100 p.s.i.g.
Reactor temperature	780° F
Space velocity	3·0 vol/vol/hr
Gas recycle rate	2000 cu. ft/brl

and the following data are typical of the results obtained when operating under these conditions.

Tractor Fuel

	Feedstock	Product *
Specific gravity at 60° F/60° F	0·824	0·820
I.B.P., ° C	154	147
10% vol at ° C	169	165
50% vol at ° C	195	194
90% vol at ° C	238	234
F.B.P., ° C	267	257
Sulphur, % wt	0·645	0·106
Sulphur removal, %	—	83·6
Colour Saybolt	+10	+21
Corrosion (Cu strip at 100° C)	Passes	Passes
Octane number (M.M.) clear	43·5	47·0

* Approximately 1·5 per cent volume bottoms were removed in the knock-out tower.

Naphtha for Petroleum Spirit (White Spirit) Production

	Feedstock	Product
Specific gravity at 60° F/60° F	0·78	0·78
I.B.P., ° C	150	145
10% vol at ° C	158	158
50% vol at ° C	170	170
90% vol at ° C	190	189
F.B.P., ° C	208	211
Sulphur, % wt	0·143	0·003
Sulphur removal, %	—	97·9

Kerosine (burning oil) has been processed under similar conditions, and gave the following results:

	Feedstock	Product *
Specific gravity at 60° F/60° F	0·794	0·793
I.B.P., ° C	160	155
10% vol at ° C	174	177
50% vol at ° C	197	197
90% vol at ° C	230	229
F.B.P., ° C.	248	247
Flash point, ° F	*ca* 120	*ca* 100
Total sulphur, % wt	0·27	0·004
Sulphur removal, %	—	98·5
Char value, mg/kg	20	12
Colour Saybolt	+25	+30

* *Ca* 1% bottoms removed in knock-out tower.

Since the commissioning of the unit, runs of 1000 hours duration without regeneration have been carried out on tractor fuels.

Utilities

The consumptions of utilities in the 3500-b.s.d. commercial unit at Llandarcy, when operating under full design conditions, are:

150 lb steam	5000 lb/hr (net)
Cooling water	20,000 I.G/hr
Fuel	25 million B.Th.U/hr
Electric power	10 kW

In this plant, the recycle gas compressor is driven by the steam generated in the waste-heat boiler.

Investment Costs

The 3500-b.s.d. commercial plant had a total erected cost within battery limits of approximately

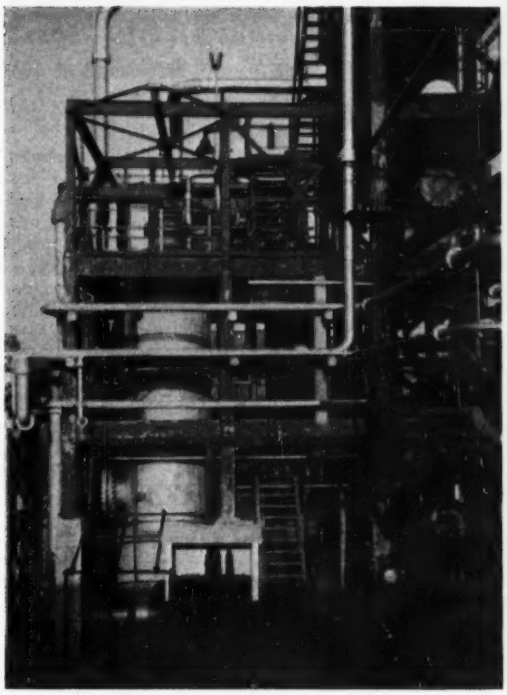

FIG 13
REACTOR (*left*) AND PRODUCT COOLERS (*top right*)

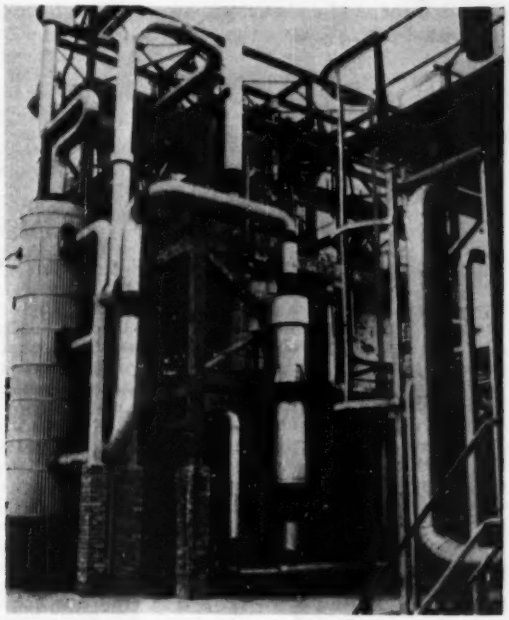

FIG 14
KNOCK-OUT COLUMN (*left*) AND WASTE-HEAT BOILER (*centre*) WITH REACTOR (*right background*)

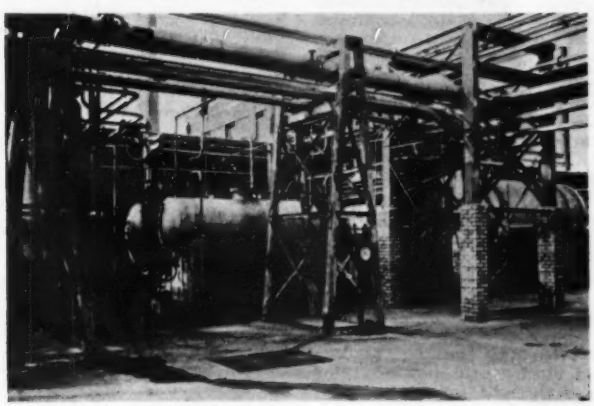

FIG 15
COALESCERS (*extreme left*), CAUSTIC SODA VESSELS (*left centre*), SEPARATOR (*right*), AND CONTROL AND PUMP-HOUSE IN BACKGROUND

£250,000. Of this total cost, materials, including common building materials, draughting engineering, procurement, and contractors' overheads and profits, amounted to £196,500.

ACKNOWLEDGMENT

The author wishes to thank the Chairman and Directors of the Anglo-Iranian Oil Co. Ltd. for permission to publish this paper and to express his appreciation of the assistance given by his colleagues in the development of the process.

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DISCUSSION

Dr L. Belchetz: The great expansion in the refining industry in the U.K. on the basis of M.E. crudes has brought us face to face with the problem of coping with products containing relatively large quantities of sulphur. Any new process which effects a reduction in sulphur content, either to improve the performance of the product or to avoid its degradation to fuel, is worthy of the closest attention.

There may be considerable argument as to whether large sums of money should be expended to lower, say the sulphur content of straight-run gas oil distillates: there is no financial incentive for doing so, and, moreover, there are alternative methods of mitigating the deleterious effects of sulphur. However, there are cases where sulphur reduction can be economically justified. I have in mind especially the process for the manufacture of premium grade kerosine from high sulphur feedstocks by Edeleanu extraction. The economic attractiveness of this process would be seriously affected if the only means of disposing of the high sulphur extract were to blend it off to fuel. However, as Mr Porter has explained, the desulphurization of this product would enable it to be used as a high octane number component in tractor fuel, and its value therefore considerably enhanced.

Hydrodesulphurization, as it has been known up to now, is an expensive process, mainly on account of the high cost of manufacturing hydrogen, and one hesitates to install such facilities unless forced to do so by competition or unless one has on hand low cost by-product hydrogen from a catalytic reformer, for example. Under these circumstances it might be preferred to use some other type of desulphurization process—*i.e.*, one capable of dealing with feedstocks of a very much wider range of molecular weight and composition than those which formed the subject of the present paper. Ready availability of cheap hydrogen, however, is the exception rather than the rule, and the autofining process in so far as it is self-supporting with respect to hydrogen and offers a means of reducing sulphur in an important range of distillates, must be regarded as a development of the greatest significance.

I must say I was very impressed with the most careful way in which the process was developed from the laboratory scale to the plant—clearly no chance of error was risked in the scaling up of the process. The final result certainly justified the pains taken.

I am somewhat surprised to note that the reactor employed is simply a mild steel vessel protected by brick lining. I should have thought in bringing the plant on stream from cold, the expansion might have resulted in cracking of the brick lining and exposure of the steel to the action of hot hydrogen containing H_2S. It would be of very great interest to us if Mr Porter were free to tell us how the reactor in the 3500-b.d. unit has, in fact, behaved in service.

F. W. B. Porter: As regards the large scale reactor, we were very careful to ensure that the preliminary heating was not too rapid. We had no trouble on the reactor for the first nine months, but then a few hot spots developed on the reactor shell. After twelve months operation the catalyst was removed to examine the lining and a few superficial cracks were found, one or two of which went down to the shell itself. These cracks were subsequently re-pointed and the catalyst replaced; subsequent operations have shown that the shell temperature is practically the same as when the reactor was first erected. Dr Thornes, of the Llandarcy Staff, may be able to give a little more detail of the inside of the reactor and the extent of the cracks in the lining. This was the only trouble experienced and that was after approximately twelve months operation.

Dr L. S. Thornes: When the reactor was examined there were cracks in the refractory lining, and in one case the parent metal on the reactor shell was exposed for approximately 3 or 4 inches square. When the metal had been cleaned down and the scale taken off there was little corrosion of the metal itself. I personally think that the refractory lining of the reactor is very satisfactory.

J. W. Hyde: There is a great deal of experience available to enable one to design this type of lined reactor, which is not novel. If the rules are followed properly in the design of the shell, and in the placing and securing of the lining, no difficulty should be experienced.

A. J. Goodfellow: Dr Belchetz referred to the very wide molecular weight range covered by this process. In examining this comment, I notice from Table VI that the sulphur removal from gas oil is only 50 to 52 per cent compared with at least 90 per cent in the other tables. I am reminded of the recent paper by Mr Rampton and his co-workers on methods of hydrocarbon analysis, in which he showed that cuts in the gas oil range have a peak of sulphur content, I believe in the range of 280° to 300° C. The percentage of sulphur present could account for about 10 per cent of material as a sulphur compound at that point. Have hydrocarbon type analyses been carried out after autofining and do they indicate that the process is selective?

F. W. B. Porter: A survey of the sulphur contents of an autofined gas oil over narrow boiling ranges has been carried out. I am not certain of the width of the cuts themselves, but in all cuts the percentage desulphurization was the same. There was no evidence that there were peaks of residual sulphur in the autofined product in the gas oil boiling range.

H. C. Rampton: As regards the sulphur content of the gas oil, provided 20° C fractions are used, the level rises fairly consistently, that is, there is no concentration of sulphur compounds at any particular boiling point. Also, the desulphurization proceeded fairly uniformly throughout the boiling range, the percentage effect being virtually the same at both ends of the scale—there being no selective desulphurization.

Dr L. Belchetz : When I referred to a wide range of molecular weight, I was thinking of an alternative desulphurization process which was capable of dealing with products in the lubricating oil range and flash distillate feed to a catalytic cracker.

A. J. Goodfellow : Am I right in assuming that if the process is not selective then the reason for the lower sulphur removal in the gas oil range is that a ceiling is set to the process conditions by the cracking temperature?

F. W. B. Porter : Regarding the ease of desulphurization of the various boiling ranges, it is, generally speaking, easier to desulphurize the lower boiling compounds than the higher ones. For example, it is much easier to desulphurize the sulphur compounds in the naphtha boiling range than the gas oil boiling range. It is probably due to the change in the sulphur compounds themselves, although little is known about the actual form of the sulphur compounds in the gas oil boiling range. We have found, for instance, that above approximately 350° C end point the sulphur compounds change in their response, not only to this process but to the hydrofining process as well. We have found that the hydrogen consumption in the hydrofining process goes up very considerably for each 1 per cent sulphur removed when the 350° C end point in the gas oil boiling range is exceeded. So the ease, or the severity of the operating conditions, changes with boiling range. The conditions under which over 90 per cent sulphur removal can be obtained with naphtha fractions only permit the removal of 50 per cent sulphur with gas oil fractions. But there is another way of looking at it. In the gasoline boiling range only 0·07 g of sulphur per 100 g of feedstock have to be removed, but in the gas oil boiling range 50 per cent removal means that 0·5 g of sulphur per 100 g of feed have to be removed. So that actually more sulphur expressed as weight of sulphur removed is taken out, although when expressed as percentage desulphurization it may not look as efficient.

In the gas oil boiling range, to increase the desulphurization one has to resort to lower space velocities. If you halve the space velocity, from 2 to 1 vol/vol/hour, the desulphurization is increased from 50 to 70 per cent. Another alternative is to resort to equilibrium pressure operation.

J. H. G. Plant : Is the process of sulphur removal wholly catalytic? Regarding the regeneration stage, I think you said that the spent gases leaving the hot catalyst contained sulphur dioxide, which would suggest that to some extent the molybdenum and cobalt oxide mixture may react as a reagent and retain some sulphur. Is it a fact that the sulphur removal from the ingoing feedstock is wholly represented by the hydrogen sulphide leaving with the products, or is the removal of sulphur during the working cycle partly catalytic and partly fixation by reaction with the catalyst mass?

F. W. B. Porter : In both hydrofining and autofining processes if the start is made with an oxide catalyst it gradually gets converted to a sulphide catalyst. With gas oil feedstocks, for instance, the catalyst is completely sulphided within a period of 5 to 15 hours, depending upon the sulphur content of the feedstock. There is, therefore, a certain amount of sulphur removed by this reaction. If, for example, a very low sulphur gasoline of 0·01 per cent wt sulphur is used, the sulphur would probably all go on the catalyst for the first 200 to 300 hours. In the hydroforming process, which uses a molybdenum oxide catalyst, the on-stream period is only 6 hours, and during that time no hydrogen sulphide was present in the product, solely because part of the catalyst had been converted to sulphide.

In the autofining process, with gas oil feedstock, we get about 5 per cent wt of sulphur on the catalyst by the end of the processing period. This value is reached in 5 to 15 hours, and then remains constant. The amount of sulphur on the catalyst depends upon the partial pressure of H_2S in the system, and this sulphur is removed during regeneration at the end of each processing period. There is therefore a certain amount of sulphur removed by this means, but it is negligible when you consider the total sulphur removed during a processing period of 200 hours with gas oil feedstocks or 1000 hours with vaporizing oils. The sulphiding step is probably very necessary, as it has been found that sulphided catalysts are better dehydrogenating and desulphurizing catalysts than the oxide type. In any case the oxide type probably cannot exist in an atmosphere of H_2S.

I. Cameron : Mr Porter, in his description of the 3500-brl unit, pointed out that a separate furnace was necessary for heating the recycle gas because the corrosive nature of the gas necessitated the use of stainless-steel tubes.

From the point of view of reducing the capital cost of the plant, was consideration given to using one furnace for both oil feed and recycle gas, but incorporating a separate circuit in stainless-steel tubing for the gas?

F. W. B. Porter : I am not an expert on the design of furnaces, but I believe the point mentioned has been considered. One of the drawbacks would be that during the regeneration step both sets of tubes would have to be heated, although only one set would be required for heating the steam. It would therefore be necessary to circulate oil through the other set of tubes during the regeneration period, which is not a good thing.

The President : In Mr Porter's paper we have a contribution of very great value. As Dr Belchetz himself said, the desulphurization of oil is a very important subject. I can only speak about the problem in connexion with crude oil, but I am greatly impressed by the possibilities of the autofining process. A few days ago I was privileged, when I was in Llandarcy, to see the full scale plant working. A plant in a modern refinery is usually a very complicated piece of equipment, but the autofining plant appears to me to possess the great merit of simplicity, and I think that on that account autofining is one of the most important advances made in recent years. After hearing the results obtained in treating distillates, my mind turned at once to the possibilities of treating crude oils and residues, because if an efficient and cheap method of desulphurizing crudes and residues can be developed, it will make a tremendous difference to the utilization of crudes from the Middle East. All Middle East crudes, unfortunately, carry a large percentage of sulphur, and on the producing end we are being continually pressed by our refining friends to discover crudes with lower sulphur contents. It is a very real problem, and there is a tendency to draw more heavily on those fields whose crude has a low sulphur content. Although the production of low sulphur content residues is of extreme importance to many industrial processes in the U.K., not least in the making of steel, the autofining process also provides a readily available source of sulphur.

I am sure you will all join with me in thanking Mr Porter very much indeed for presenting his paper tonight. I think this occasion will be a landmark in petroleum refining, and possibly also in the development of suitable crude oils, for if we can improve the quality of the petroleum reserves in the Middle East, it will be a very big step forward indeed. I therefore hope that it will not be long before Mr Porter or one of his colleagues comes to tell us of the progress they are making in the desulphurization of crude oils and residues.

The vote of thanks was accorded with acclamation.

FINAL REPORT ON THE FIELD EXPOSURE TEST CONDUCTED BY THE IP PROTECTIVES PANEL

SUMMARY

In connexion with its work on the development and standardization of a laboratory method for assessing the corrosion-preventive properties of temporary protectives, the Protectives Panel has conducted a field test in which mild steel panels coated with various types of protective were exposed at a number of sites whose atmospheric conditions were widely divergent. The primary object of this test was to rank the protectives in their order of merit and thus afford a basis on which to judge results obtained by the various laboratory methods. A secondary object was to ascertain whether differences of environment affected the order of merit of the protectives.

Analysis of the final results shows a satisfactory degree of concordance, and it would appear that the environment does not play an important part in determining the *order* of failure, although, of course, it has a considerable effect on the *rate* of failure.

INTRODUCTION

OBVIOUSLY the most important property of a temporary corrosion preventive is its ability to protect metal against rusting. There are several laboratory tests in existence for assessing this property, but none is sufficiently widely accepted to warrant its immediate adoption as a standard method, nor is there much evidence as to whether such tests do in fact truly reflect the behaviour of temporary corrosion preventives in practice. It was therefore decided to investigate the more promising methods with a view to standardization. Before this could be done, however, it was necessary to rank a series of protectives in their order of merit by means of a simulated field test so as to obtain a yardstick for the evaluation of the laboratory tests. It was decided that the most suitable type of test would be one in which coated panels were exposed to atmospheric conditions but sheltered from direct sun and rain; such a test was expected to be sufficiently severe to give results in a reasonable time and yet discriminating enough to differentiate between the various types of protective. Furthermore, since it had been suggested that the order of merit might be different for different environments, it was decided to conduct the tests at sites having atmospheres as widely divergent as possible (*i.e.*, urban, industrial, rural, and marine).

This report describes the conduct of the test and discusses the results obtained.

SELECTION OF SITES

Brief details of the twelve exposure sites selected for this test are given in Table I. It will be observed that 6 of these are classed as "industrial" locations, 2 as "industrial marine," 2 as "urban," 1 as "rural," and 1 as "marine." It was originally intended that the sites at Amsterdam and Hull should represent marine conditions, but it was later realized that this was not the case, since the exposure sites were some distance from the open sea, and prevailing winds tended to blow off-shore. An additional test was therefore run at a truly marine site at Birkenhead.

TABLE I

Details of Exposure Sites

Location	Classification	Description of exposure shed *
Abingdon	Rural	Underneath the overhanging eaves of a small thatched building in the grounds of an estate occupied by a research laboratory.
Amsterdam	Industrial/marine	A specially constructed louvred cabinet approx 4-ft cube to U.S. Army–Navy spec AN-C-52a, para F-4-d(2)e.
Birkenhead	Marine	In the roof beams of a quayside loading bank facing W.
Doncaster	Industria	Immediately under the roof of an open-fronted cycle-shed in a railway engineering works.
Fulham	Industrial	Under the corrugated-iron roof of a well-ventilated brick-built shed on a petroleum depot.
Hull	Industrial/marine	In the rafters of an open-sided loading bay facing a quay.
Sunbury	Urban	Under a sloping roof of felt, sited in the angle of two parapet walls on the flat roof of a building 30 ft high; open side facing S.W.
Teddington	Urban	In a specially constructed "exposure shed." The lower 3 ft of the walls consisted of wire netting, and the panels were suspended at about 6 ft from the ground.
Trafford Park	Industria	Under the asbestos roof of a stillage shed at an oil refinery.
Vauxhall	Industria	In the louvred top of a disused shed on a petroleum depot.
Wandsworth	Industrial	Suspended from the ceiling of a flat-roofed brick passage-way 12 ft long, and open at both ends.
Woolwich	Industrial	Under the corrugated-iron roof of an open-fronted cycle-shed at Woolwich arsenal.

* In all cases care was taken to ensure that the panels were not exposed to direct sun or rain.

SELECTION OF MATERIALS

Panels

After careful consideration it was agreed that the most representative and reproducible test panels would be of cold-rolled mild steel conforming to BS 970 En2a/1; it was appreciated that the results obtained might not be applicable to other metals (*e.g.*, cast iron). Sufficient 6-inch × 4-inch × 18 BG panels for the whole programme were obtained from Messrs. Richard Thomas & Baldwin Ltd., who guaranteed that they were all cut from the same batch of steel.

Protectives

The following protectives were selected as being representative of the main types of petroleum-based protectives in common use :

(i) soft film solvent-deposited type (DTD 121D);

(ii) soft film hot-dipping type (petrolatum with and without glyceryl mono-oleate);

(iii) hard film solvent-deposited type (CS 1033B and CS 1033D);

(iv) oil type (CS 1663C and CS 1663F).

Since it had been stated that the most frequent cause of failure of a protective was thinness of the film, it was decided that the DTD 121D, the CS 1033D, and the two petrolatums should also be diluted so as to obtain abnormally low film-weights (see section on application).

The compositions of all these protectives are given in Table II.

TABLE II

Coating of Panels

Ref.	Composition of protective	Method of application
a	DTD 121D (1 part lanoline, 2 parts white spirit).	Dip at room temperature for 5 sec, withdraw over 3 sec.
b	Diluted DTD 121D (1 part lanolin, 9 parts white spirit).	As *a*.
c (i)	Petrolatum.	Dip at 170°–180° F for 30 sec, withdraw over 1–2 sec.
c (ii)	Diluted petrolatum (29% petrolatum, 71% toluene).	As *a*. Allow to dry for 30 min at room temperature, then heat in oven at 95° C for 4 min.
d (i)	Inhibited petrolatum (98% petrolatum, 2% glyceryl mono-oleate).	As *c* (i).
d (ii)	Diluted inhibited petrolatum (29% *d* (i), 71% toluene).	As *c* (ii).
e	CS 1033B (24% rosin, 15% neutralized wool-grease, 58% coal tar naphtha, 3% special bitumen).	As *a*.
f	CS 1033D (18% oxidized bitumen, 12% neutralized wool-grease, 19% coal tar naphtha, 51% trichloroethylene).	As *a*.
g	Diluted CS 1033D (29% CS 1033D, 71% thinners).	As *a*.
h	CS 1663C (85% mineral oil, 10% lanolin, 5% kerosine).	As *a*.
i	CS 1663F (an inhibited mineral oil).	As *a*.

PREPARATION OF PANELS

Instructions for the preparations of the panels were as follows:

> "Panels of mild steel conforming to BS 970 En2a/1, 6-inch × 4-inch × 18 BG, free from deep pits, scratches, and surface imperfections shall be thoroughly abraded with No. 0 emery cloth on both sides finishing with a circular motion.
>
> "Immediately after abrasion they shall be fitted with a nichrome suspension wire, thoroughly cleaned and degreased by swabbing generously with pieces of clean cloth or filter paper dipped in toluene A.R. and then rinsed in methanol (74 o.p.) and dried for a few minutes in a stream of warm dry air. During and after degreasing, care must be taken not to handle the test surfaces with the naked hand."

APPLICATION OF PROTECTIVES

The protectives were applied to the prepared panels without delay in order to avoid deterioration of the metal surfaces. The methods of application were as shown in Table II, while Table III shows the weights of the coatings which were determined after allowing the panels to drain or dry for 24 hours in a dust-free atmosphere; drainage "tears" were not removed from the panels.

It was found to be impossible to obtain a uniform coating of the hot-dipped inhibited petrolatum; this material gave what came to be known as a "lace-curtain" effect. As will be seen from Table III, the weights of coating obtained with some of the other protectives also varied quite widely from site to site (and even from panel to panel at a given site). However, it was subsequently found that the omission of results obtained on the more divergent coatings had no effect on the final ranking of the protectives, and it was therefore decided to retain all such results.

EXPOSURE OF PANELS

Three sets of coated panels and 3 uncoated "controls" (36 in all) were exposed at each site. The panels were hung vertically and were inspected at intervals, the observations being recorded on a proforma. It was intended that the criterion of failure should be the appearance of at least 24 corrosion spots on one face of a panel (*i.e.*, 1 spot per square inch); any corrosion occurring within $\frac{1}{4}$-inch of the edge of the panel was to be duly noted, but was not to be taken into account when assessing failure. In some cases, however, it was very difficult to decide when failure had taken place; some coatings were either naturally rather opaque or else collected so much dust that it was impossible to detect the onset of corrosion; others did not fail in spots but in patches or even by a fairly uniform staining. Nevertheless, by frequent interchange of ideas and by occasional comparison of panels taken from the various sites, it was possible to arrive at standards of failure in such cases even if somewhat arbitrary.

The test was started on 10 August 1949 at all sites except Amsterdam and Birkenhead. On 16 September 1949 each operator removed one complete set of panels, cleaned them in hot white spirit and inspected them for signs of failure. A second set of panels was removed on 26 October 1949, and the third and final set on 18 April 1950. When each set was removed, a control panel was derusted by immersion in conc HCl containing 2 per cent antimony trioxide and 5 per cent stannous chloride and its loss in weight determined. Interim reports were issued in October 1949 and January 1950, but for the present purpose it is only necessary to consider the final position, which is discussed below.

The test at Amsterdam commenced on 18 November 1949 and continued until 30 April 1950. The

TABLE III

Weights of Coatings, g per panel

Location	*a*	*b*	*c* (i)	*c* (ii)	*d* (i)	*d* (ii)	*e*	*f*	*g*	*h*	*i*
Abingdon	0·14	0·03	2·69	0·38	2·60	0·27	0·40	0·62	0·09	0·27	0·21
	0·12	0·04	2·49	0·30	1·90	0·33	0·44	0·56	0·06	0·46	0·21
	0·13	0·03	2·02	0·40	1·53	0·34	0·52	0·61	0·07	0·28	0·18
Amsterdam	0·20	0·04	2·59	0·83	2·34	0·52	0·46	0·71	0·09	0·21	0·27
	0·20	0·04	2·68	0·71	2·31	0·58	0·49	0·60	0·07	0·20	0·18
	0·21	0·04	2·57	0·67	2·32	0·65	0·51	0·67	0·05	0·21	0·18
Birkenhead	0·15	0·03	1·21	0·39	1·29	0·49	0·45	0·14	0·10	0·26	0·30
	0·10	0·03	1·52	0·40	1·42	0·41	0·42	0·32	0·10	0·29	0·22
	0·12	0·02	2·01	0·36	1·41	0·46	0·43	0·96	0·10	0·31	0·25
Doncaster	0·16	0·03	2·77	0·36	2·29	0·36	0·45	0·64	0·07	0·35	0·15
	0·16	0·04	2·84	0·35	2·63	0·36	0·40	0·58	0·07	0·36	0·34
	0·17	0·05	2·63	0·36	2·66	0·36	0·49	0·62	0·07	0·24	0·21
Fulham	0·13	0·03	2·36	0·31	1·75	0·52	0·43	0·66	0·08	0·21	0·28
	0·15	0·04	2·15	0·39	2·20	0·46	0·44	0·66	0·08	0·25	0·19
	0·17	0·04	2·27	0·31	1·77	0·47	0·41	0·67	0·08	0·20	0·16
Hull	0·14	0·04	2·41	0·34	3·06	0·39	0·41	0·58	0·06	0·29	0·68
	0·17	0·02	2·56	0·34	2·96	0·39	0·46	0·65	0·06	0·36	0·11
	0·15	0·04	2·46	0·38	2·40	0·39	0·41	0·62	0·05	0·33	0·33
Sunbury	—	0·03	2·15	0·43	2·10	0·31	0·38	0·60	0·07	0·17	0·14
	—	0·03	2·20	0·52	1·50	0·33	0·38	0·59	0·06	0·16	0·14
	—	0·03	2·27	0·50	2·10	0·40	0·38	0·52	0·07	0·18	0·13
Teddington	0·17	0·04	2·27	0·60	2·10	1·11	0·51	0·96	0·07	0·27	0·51
	0·16	0·03	2·71	0·70	2·00	0·97	0·46	0·88	0·07	0·19	0·51
	0·14	0·03	2·37	0·68	2·39	0·99	0·48	0·84	0·07	0·22	0·52
Trafford Park	0·17	0·03	2·12	0·28	—	0·37	0·44	1·29	0·07	0·35	0·17
	0·18	0·03	1·93	0·29	—	0·37	0·43	1·18	0·07	0·20	0·16
	0·21	0·04	2·23	0·32	—	0·42	0·48	0·08	0·07	0·28	0·19
Vauxhall	0·14	0·06	2·15	0·67	2·05	0·60	0·50	0·65	0·05	0·23	0·20
	0·15	0·05	2·10	0·70	2·05	0·65	0·57	0·92	0·04	0·22	0·19
	0·14	0·05	2·17	0·65	2·05	0·64	0·45	0·70	0·04	0·20	0·18
Wandsworth	—	0·02	2·40	0·34	0·69	0·42	0·54	0·75	0·10	0·29	0·16
	—	0·02	2·30	0·29	2·02	0·52	0·46	0·80	0·09	0·38	0·16
	—	0·02	2·50	0·26	1·97	0·47	0·49	0·74	0·08	0·30	0·22
Woolwich	0·15	0·05	2·50	0·40	2·60	0·45	0·45	0·65	0·05	0·25	0·20
	0·15	0·05	2·25	0·50	2·40	0·45	0·45	0·60	0·10	0·20	0·20
	0·15	0·05	2·50	0·45	2·55	0·45	0·45	0·65	0·10	0·20	0·20
Average	0·15	0·035	2·34	0·45	2·13	0·49	0·45	0·70	0·07	0·26	0·24

Birkenhead test was started on 15 December 1950 and terminated on 27 July 1951, when all coatings had failed. The fact that this test was begun in winter instead of summer does not appear to have had any appreciable effect on the results, as will be seen later.

RESULTS OF TEST

Times to Failure and Order of Merit

The final results of the test are shown in Table IV, which gives the times to failure of the various protectives at each site. Based on these figures, an order of merit was obtained for each site, and these are shown in Table V, together with the average order of merit for all sites and the Spearman Ranking Coefficient for the individual sites. This coefficient measures the degree of concordance between the results obtained at the different sites, and it will be seen that in most cases it approaches unity, which indicates good agreement.

It will be seen that a fair degree of reproducibility was obtained with all protectives except the inhibited petrolatum. The wide variation of results obtained on this material was undoubtedly due to the unsatisfactory coatings which it gave (see section on application). It was therefore felt that it would be quite permissible to discard these results, and this has been done in Table VI. The improvement in some of the lower Spearman Ranking Coefficients is quite marked.

By courtesy of Mr van Rest of the National Physical

TABLE IV

Time to Failure, days

Location	*a*	*b*	*c* (i)	*c* (ii)	*d* (i)	*d* (ii)	*e*	*f*	*g*	*h*	*i*
Abingdon	88 †	67	>250	>250	250 †	250 †	>250	>250	67	67	67
Amsterdam	46	11	>150	>150	14	10	100	>150	76	8	18
Birkenhead	74	14	221	194	9	185	156	164	123	21	12
Doncaster	30	9	>250	250	>250	250	160	160	25	38	80
Fulham	70	18	>250	150	50	>250	>250	>250	60	15	16 *
Hull	35	14	>250	90	>250	90	120	75	21	31	42
Sunbury	100	54	195	195	>250	193	>250	160 †	113	20	20
Teddington	144	50	>250	>250	155	>250	>250	150	80	100	60
Trafford Park	19	5	250 †	90	abandoned	64	167 †	167 †	28	7	19
Vauxhall	81	47	>250	120	50	120	>250	>250	77	25	25
Wandsworth	192	23	250	192	9	192	250	250	192	49	84
Woolwich	55 *	22	174 *	77 *	22	77 *	100 *	150 *	55	22	22

* Estimated. † Failure discovered on cleaning panel; may have failed earlier.

TABLE V *

Order of Merit

Location	*a*	*b*	*c* (i)	*c* (ii)	*d* (i)	*d* (ii)	*e*	*f*	*g*	*h*	*i*	Spearman coefficient
Abingdon	7	9½	2½	2½	5½	5½	2½	2½	9½	9½	9½	0·95
Amsterdam	6	9	2½	2½	8	10	4	1	5	11	7	0·72
Birkenhead	7	9	1	2	11	3	5	4	6	8	10	0·75
Doncaster	9	11	1½	3½	1½	3½	5½	5½	10	8	7	0·74
Fulham	6	9	2½	5	8	2½	2½	2½	7	11	10	0·90
Hull	8	11	1½	4½	1½	4½	3	6	10	9	7	0·81
Sunbury	8	9	3½	3½	1½	5	1½	6	7	10½	10½	0·80
Teddington	7	11	2½	2½	5	2½	2½	6	9	8	10	0·88
Trafford Park	8½	11	1	4	6 *	5	2½	2½	7	10	8½	0·98
Vauxhall	6	9	2	4½	8	4½	2	2	7	10½	10½	0·93
Wandsworth	5½	10	2	5½	11	5½	2	2	5½	9	8	0·81
Woolwich	6½	9½	1	4½	9½	4½	3	2	6½	9½	9½	0·91
Average ranking	7	11	1	4	6	5	2	3	8	10	9	

* This test was abandoned, and so an average ranking has been given.

TABLE VI *

Order of Merit

Location	*a*	*b*	*c* (i)	*c* (ii)	*d* (ii)	*e*	*f*	*g*	*h*	*i*	Spearman coefficient
Abingdon	6	8½	2½	2½	5	2½	2½	8½	8½	8½	0·94
Amsterdam	6	8	2½	2½	9	4	1	5	10	7	0·77
Birkenhead	7	9	1	2	3	5	4	6	8	10	0·84
Doncaster	8	10	1	2½	2½	4½	4½	9	7	6	0·80
Fulham	6	8	2½	5	2½	2½	2½	7	10	9	0·90
Hull	7	10	1	3½	3½	2	5	9	8	6	0·90
Sunbury	7	8	2½	2½	4	1	5	6	9½	9½	0·88
Teddington	6	10	2½	2½	2½	2½	5	8	7	9	0·87
Trafford Park	7½	10	1	4	5	2½	2½	6	9	7½	0·98
Vauxhall	6	8	2	4½	4½	2	2	7	9½	9½	0·95
Wandsworth	5½	10	2	5½	5½	2	2	5½	9	8	0·96
Woolwich	6½	9	1	4½	4½	3	2	6½	9	9	0·97
Average ranking	6	10	1	4	5	2	3	7	9	8	

* Omitting hot dipped inhibited petrolatum *d* (i).

Laboratory, the rankings of the various protectives at the different stations were examined :

(*a*) by comparing them with the average ranking for all eleven stations (termed the field ranking);

(*b*) by comparing variability of rankings among themselves.

The first comparison made use of the Kendall Rank correlation coefficient and the second the coefficient of concordance.

It was found, when comparing the ranking of each station with the average or field ranking, that the agreement was reasonably good for seven stations, that the apparent agreement could quite well have been a chance effect at three other stations (Amsterdam, Hull, and Sunbury) and that at one station (Doncaster) there was disagreement. In view of the difficulties or corrosion testing it was felt that these findings could be regarded as encouraging.

The test for concordance of rankings amongst themselves was also encouraging, and the significance test indicated that the amount of concordance ($W = 0{\cdot}738$) * found was most unlikely to have occurred by chance.

Loss in Weight of Control Panels

Table VII gives the loss in weight of the control panels which were derusted on the dates shown. It will be seen that in some cases the results are rather unexpected. In particular, it is surprising that the panels exposed at the urban site at Teddington should lose more than twice as much as the panels at most of the industrial sites. It is suggested that this may be due to the fact that in industrial areas the rust was held on to the panels with a coating of grime, and so formed a protective coating; in urban areas, on the other hand, the rust fell from the panels and exposed fresh surfaces to attack. It would be interesting to learn whether other observers have noticed this effect, and, if so, whether any other explanations have been offered.

TABLE VII

Loss in Weight of Control Panels

Location	Loss in weight of panel on de-rusting after period shown		
	37 days	77 days	250 days
	g	g	g
Abingdon	—	1·61	—
Amsterdam	0·46 (13 days)	1·29 (36 days)	2·75 (75 days)
Doncaster	1·05	2·27	7·95 (300 days)
Fulham	0·87	1·34	—
Hull	1·24	2·75	10·81 (300 days)
Sunbury	0·54	—	2·07
Teddington	2·6	5·0	7·8
Vauxhall	0·47	1·10	—
Wandsworth	—	2·11	—
Woolwich	2·08	4·4	—

CONCLUSIONS

It is the considered view of the IP Protectives Panel that the results of this test indicate that whereas the environment played a large part in deciding the rate of failure of the protectives, it does not appear to have materially affected the order in which they failed. It is also felt that these results will serve as a useful basis for the evaluation of laboratory tests.

* W measures in a sense the communality of judgment of the observers at the various stations. $W = 1$ would indicate complete concordance, whereas $W = 0$ would indicate complete discordance.

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A full description of the Phillips detonation meter appears in the 1952 edition of the ASTM Manual of Engine Test Methods for Rating Fuels and a note summarising the reasons for the adoption of the meter as standard instrumentation is given in *ASTM Bulletin No.* 83, dated July 1953. The advantages claimed for the meter have been confirmed by co-operative tests organized by the IP Knock Rating of Aviation Fuel and Knock Rating of Motor Fuel Panels.

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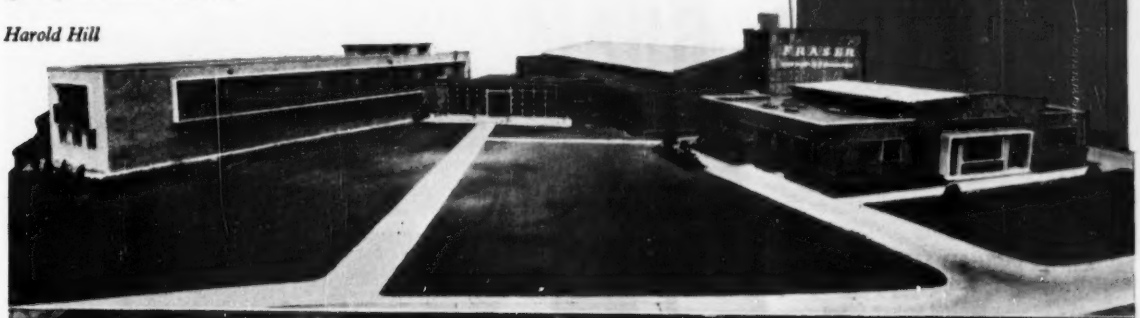

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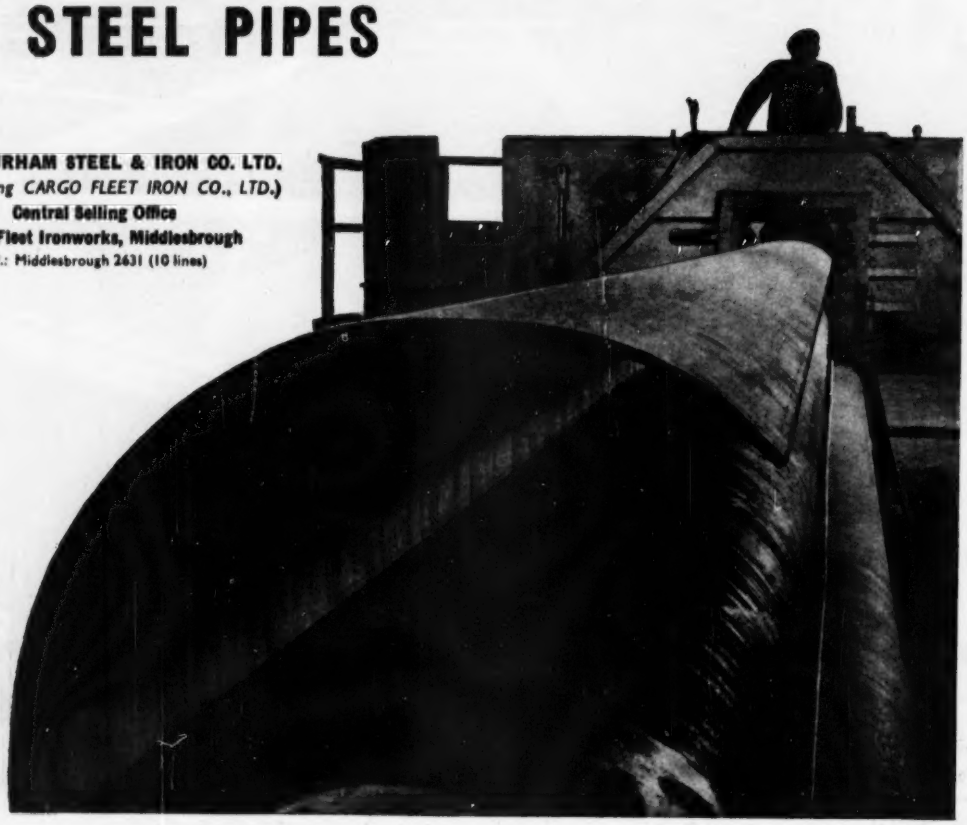

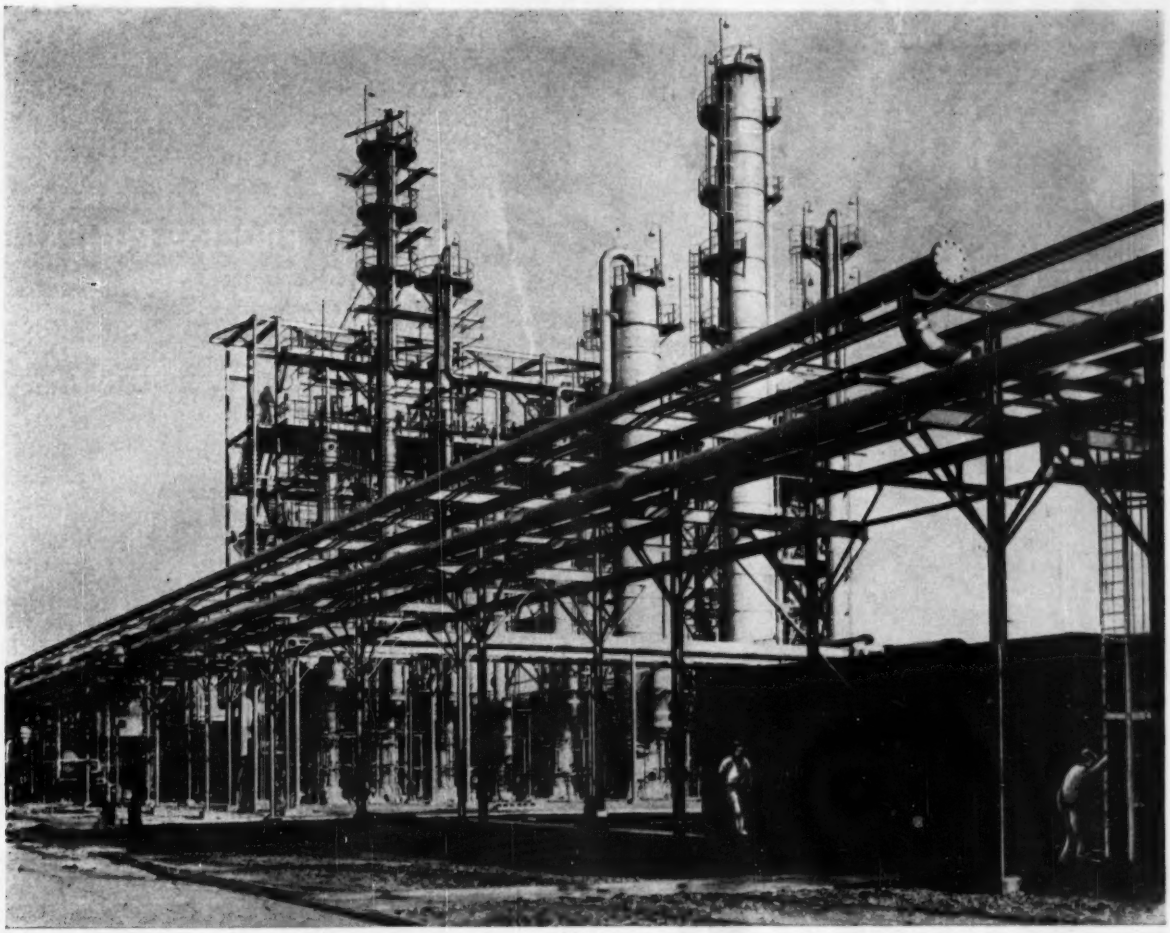

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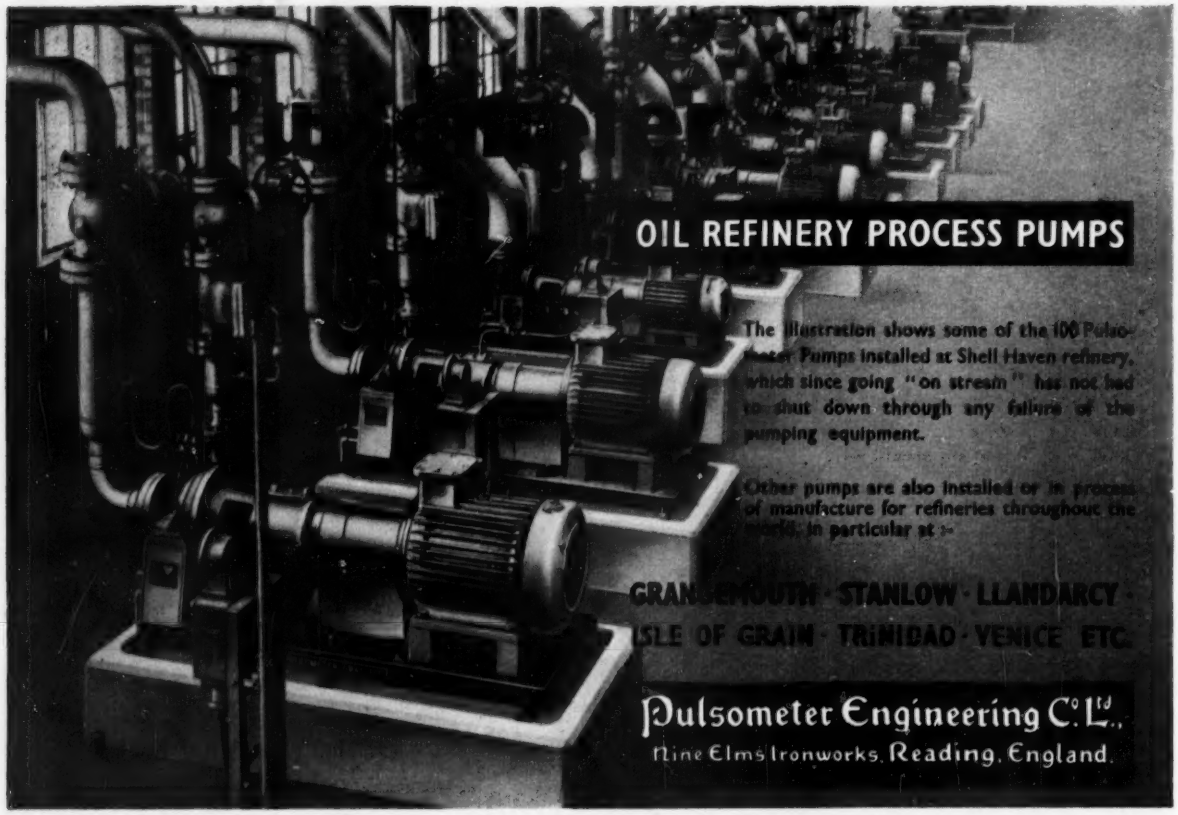
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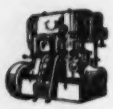

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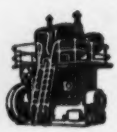

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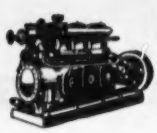

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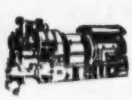

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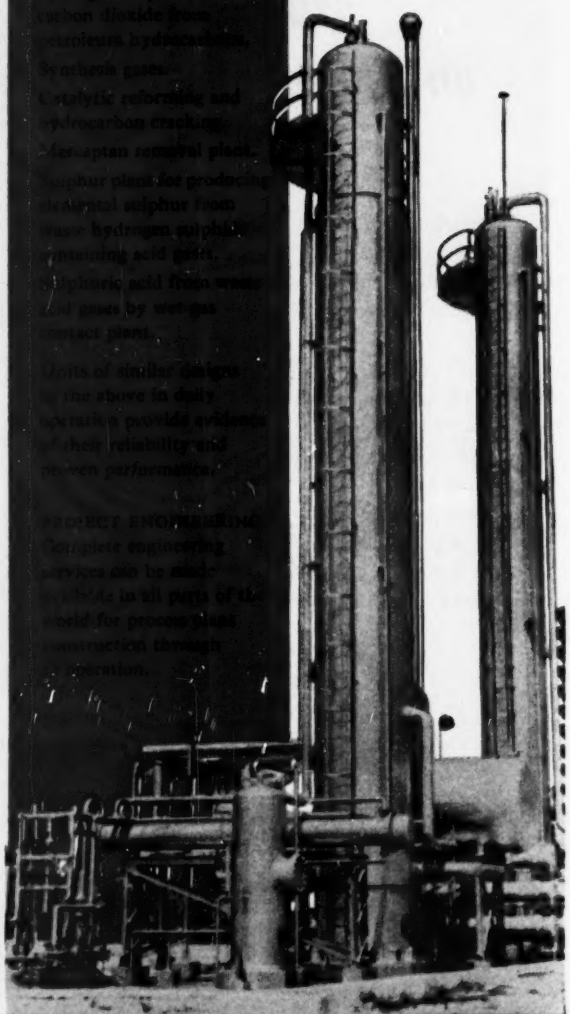

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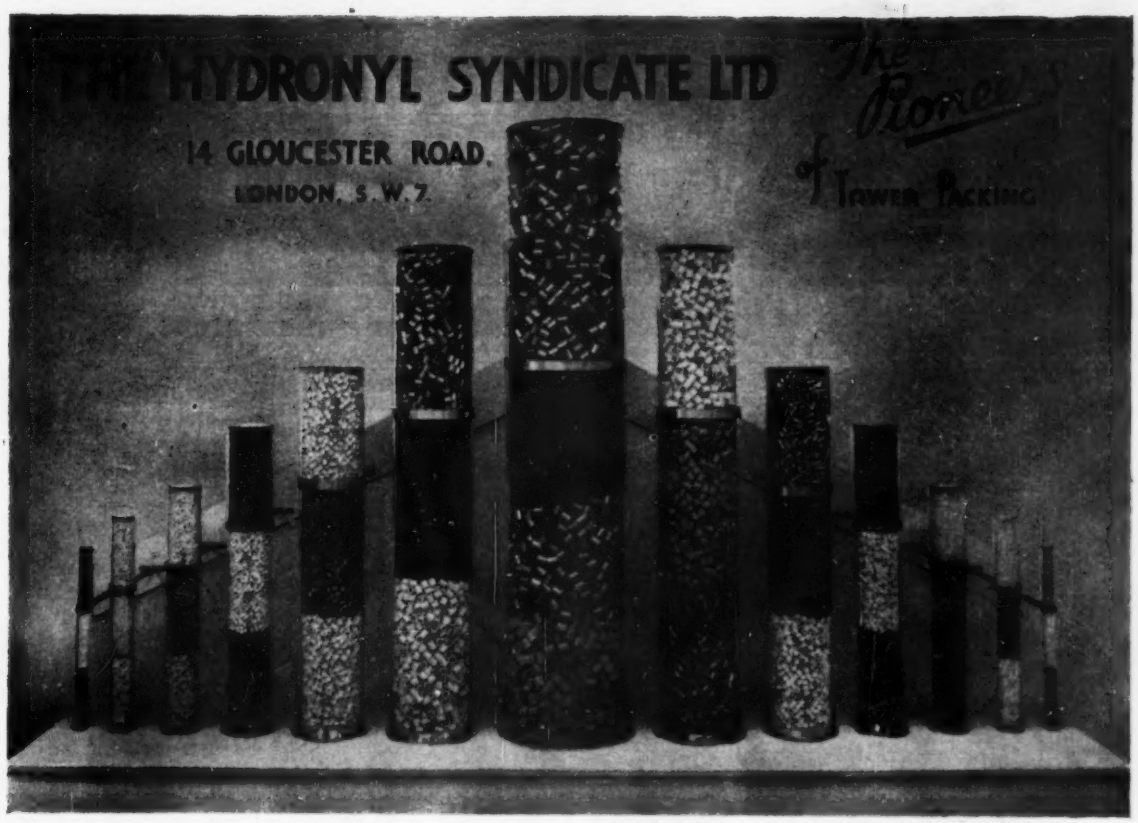

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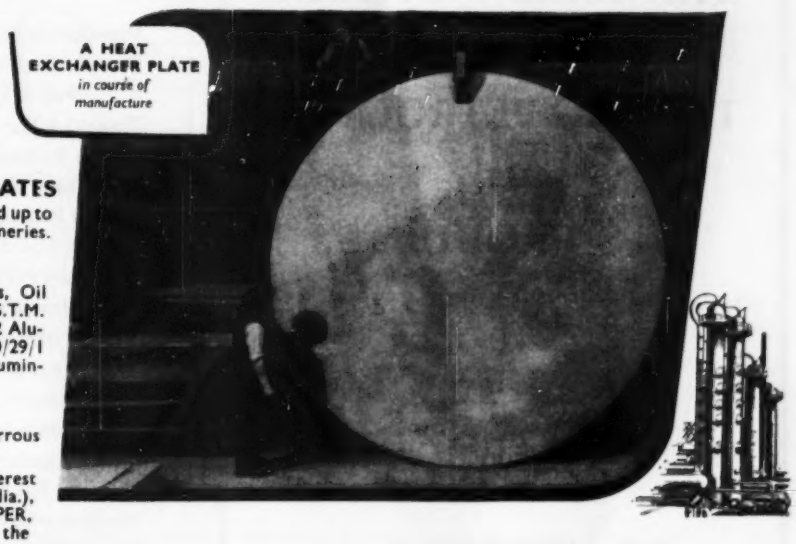

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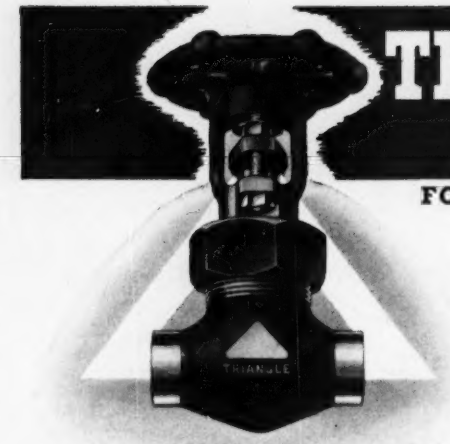

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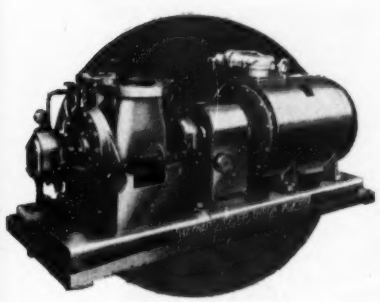

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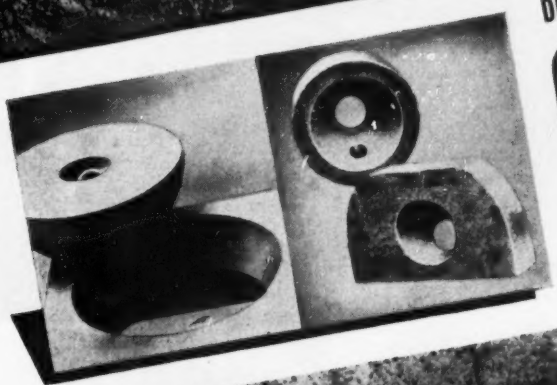

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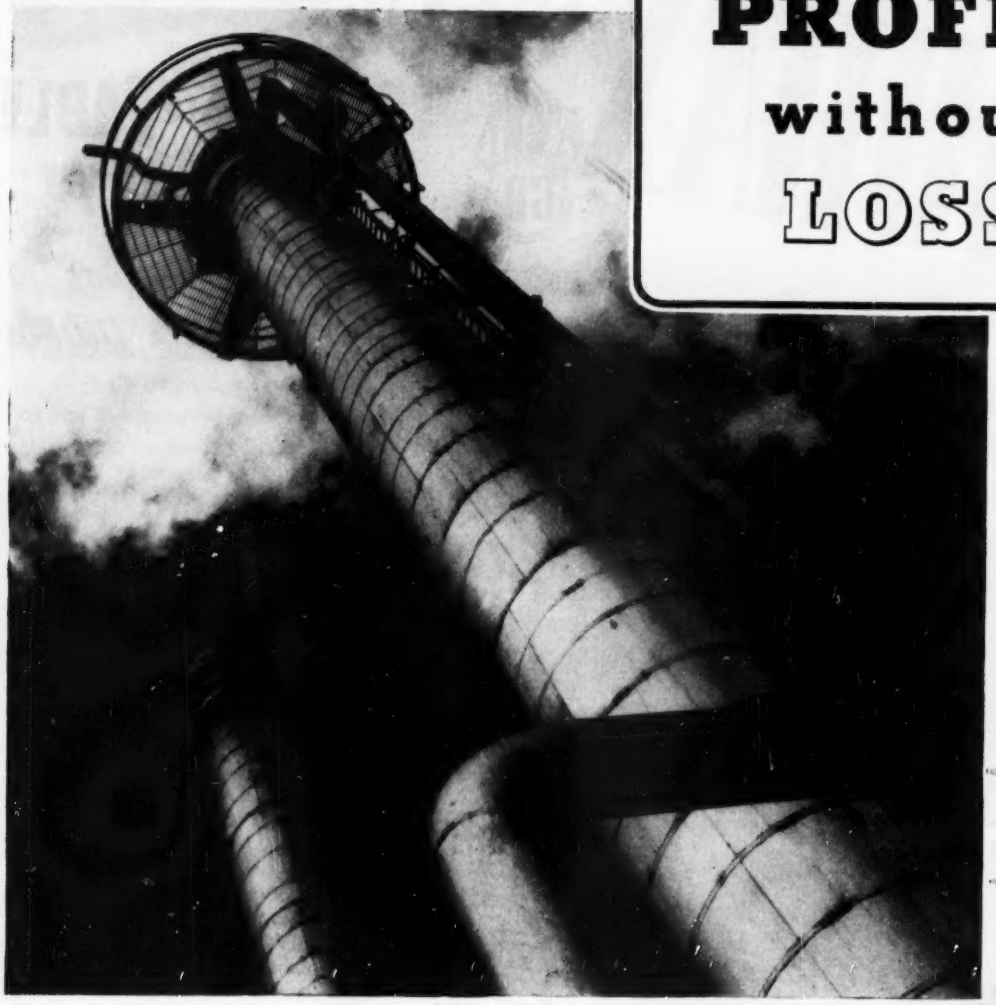

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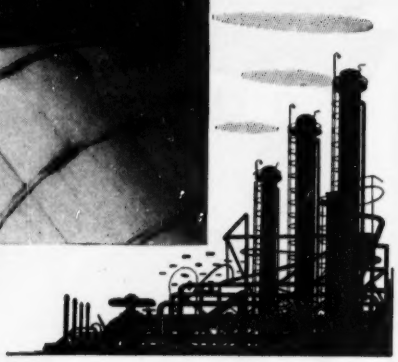

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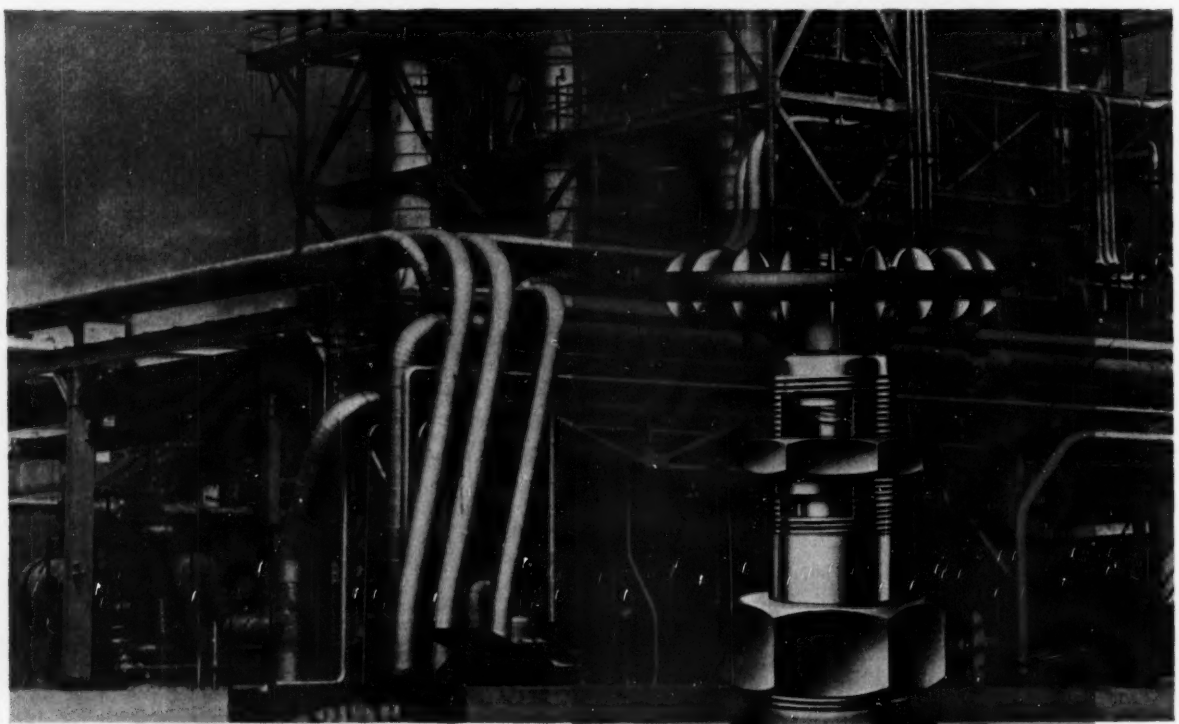
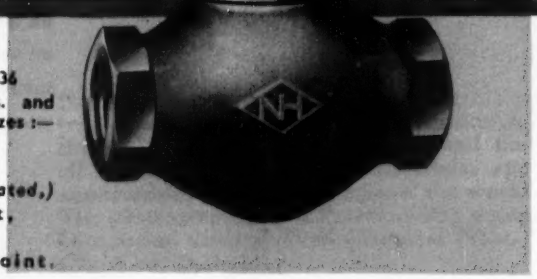


A SHELL PHOTO



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